B. A. MIRTOV

GASEOUS COMPOSITION OF THE ATMOSPHERE

and its Analysis

TRANSLATED FROM RUSSIAN

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GASEOUS COMPOSITION OF THE ATMOSPHERE and Its Analysis

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Translation Editor's Note

Most of the names of scientists mentioned in this book have been rendered in their English form. However, in those cases in which the original could not be traced some form of transliteration has been made from the Russian.

PREFACE

The problem of the gaseous composition of the atmosphere is one of the central questions of modern atmospheric physics. We need not consider in detail the fact that the gaseous composition, which varies considerably with height, has a vital influence on most phenomena occurring in the Earth's atmosphere. In the upper layers of the atmosphere, there is no single problem (with the possible exception of the wind conditions) which can be solved accurately without a knowledge of the chemical nature of these layers.

As far as I know, this is the first book to appear in either Russian or foreign literature which attempts to collect and systematize the large amount of work devoted to the investigation of the composition of the Earth's air cover. Hundreds of papers, not connected by any unifying idea, some of them old and undeservedly forgotten and others scattered throughout various journals, cannot give a complete impression of the gaseous composition of the atmosphere. The scattered nature of the material makes it necessary to spend a large amount of time and trouble just to become acquainted with the work which has been done.

The absence of a critical appraisal of the often somewhat contradictory results of various experiments has led to the inclusion of incorrect information in modern courses on atmospheric physics and in most reference books. This has happened even when dealing with the lower atmosphere which has been most thoroughly investigated.

The recent use of rockets and artificial satellites has led to rapid progress in our exploration of the upper atmosphere. The large amount of very interesting material, which has accumulated within the short space of the last decade, needs analysis and detailed commentary. All these considerations have led me to write this monograph, in which I have tried to collect and critically discuss the existing experimental material on the chemical composition of the atmosphere.

This book deals with a series of problems connected with the investigation of the composition of the atmosphere, but it is by no means my intention to try to describe all sides of this subject. In order to avoid giving the reader a false impression of the volume of work discussed, I shall now clearly define the range covered.

I have omitted practically all discussion of indirect methods of determining the composition, and the results obtained from them. Among these methods I include the obtaining and identification of visible spectra of the night sky and of the aurora borealis and australis. A number of works of a theoretical nature, dealing with the investigation of elementary processes in the upper atmosphere (dissociation, recombination and ionization processes, etc.), are also not discussed. These investigations form an independent field of knowledge, and I shall only refer to them when necessary. Nor shall I deal with work on the problem of the geological past of the Earth's atmosphere.

There is no doubt whatever that the composition of the atmosphere has changed considerably due to processes taking place in the biosphere during the period of the Earth's existence. It is quite likely that extremely slow changes of global character are still taking place today; however, these changes are so negligible that we can safely regard the Earth's atmosphere as already having reached a state of (dynamic) equilibrium throughout the whole period of investigation.

The chapter on the ozone content of the atmosphere was written by G. S. Ivanov-Kholodnyi. The new data given in this chapter were all obtained from direct rocket measurements. Because of the different experimental methods used in these investigations, this chapter is given separately, in the form of an appendix.

This book does not include material connected with the presence of water vapor in the lower atmosphere. A large number of papers have appeared on this subject, to which the reader is referred.

The chemical composition of the atmosphere embraces three branches of science (physics, chemistry and geophysics), and specialists from all three branches must therefore take part in these investigations. It is interesting to note that as our knowledge of the atmosphere has grown, the center of gravity of the investigations has gradually shifted from chemical to physico-chemical methods, and finally to physical ones. The investigation of the variations of the gaseous composition of the atmosphere in space and time has always been a part of geophysics.

As we shall see below, the first investigations of the air were carried out by chemists. Then, when it became necessary to investigate the low concentrations of inert gases present in very low-weight samples taken from high altitudes, physical chemists were also needed. Finally, for investigating the composition of the upper and outer atmosphere use was made of powerful methods of modern physics such as spectroscopy and mass spectroscopy.

All these methods will be discussed in this book. The use of each one was dictated by the particular problems to be solved, and was justified by the general historical development of science.

The most important problem in the study of the composition of the atmosphere is the question as to how this composition changes with the height above the surface of the Earth. Closely linked with this is the question of the height at which gravitational separation of the gases occurs. This book will be mainly devoted to answering these questions on the bases of the results of experimental investigations.

The investigation of the composition of the Earth's atmosphere at various heights was begun more than 150 years ago. The impetus to studies of this kind was given by Dalton in 1802, when he put forward the law of partial pressure and of gaseous diffusion. According to this law, air, which is a mixture of light and heavy gases, should increase its percentage of light gases at the expense of the heavy gases at higher altitudes above the Earth.

There is, however, a powerful factor in nature (i. e., mixing due to convection and turbulence) which prevents the atmospheric gases from obeying Dalton's law. The degree of mixing decreases with height; therefore there should be a certain height above which the gravitational separation

of the gases predominates over the mixing processes. The problem of determining this height is a very difficult one, and has not yet been solved with necessary accuracy and completeness.

Investigators have found that this boundary begins at an altitude of about 100 km. Starting from this height, it is possible to observe a rise in the relative concentration of nitrogen in the Earth's atmosphere compared to that of argon, while below this height the atmospheric gases are completely mixed. This means that the problem of the whereabouts of the boundary between the regions of gravitational separation and mixing, which had seemed a simple one in Dalton's time, "suddenly" lost all its simplicity and clarity. The height of this boundary is such that there is considerable dissociation of oxygen due to the shortwave solar radiation. This leads to the formation of unstable and chemically active atoms and radicals (O, NO, OH, etc.).

This naturally complicates the picture of the distribution of oxygen with height. If above a given height in the atmosphere molecules begin to dissociate to atoms, which recombine to form molecules of a different type, and if the limiting heights within which these new molecules can exist are determined by other physical conditions, then the simple law of gravitational separation will clearly be complicated by factors determining the "life" of the given gas at a given height.

While we can still talk of an "exact" height of gravitational separation for gases such as nitrogen and argon (which are not appreciably affected at these heights), i. e., that transition height above which the atmosphere begins to be deficient in argon, this way of formulating the problem clearly loses its significance for oxygen.

The problem of determining the boundary of gravitational separation in these high regions of the atmosphere is complicated still further if a considerable proportion of ions are present as well as electrically neutral gases. In the exosphere, for example, where the mean free path is relatively large and the number of ionized particles considerable, the distribution of the neutral atoms and molecules with height may differ from that of their ions owing to the effect of the Earth's magnetic field on the motion of the charged particles.

After these introductory remarks we could proceed at once to a systematic discussion of the past and present investigations. However, we thought that it might be useful to give first a very brief account of present-day knowledge of the gas composition of the atmosphere.

We know most about the composition of the lowest layers of the atmosphere (those nearest the Earth), since here there is no problem of carrying the measuring equipment up to the desired height. Despite this, however, extensive "world-wide" experiments were finished only 20–30 years ago. Similar experiments (determination of the CO_2 content of the lower atmosphere) were carried out in Antarctica in 1958. These measurements provided further confirmation of the view that the composition of the air near the Earth is constant at all points on its surface.

The composition of the atmosphere as a function of height has been studied much less. However, the variation up to an altitude of 50 km may be taken as known by now, except that a certain amount of work needs to be carried out on ozone and water vapor at this altitude.

The situation for the layer from 50-100 km above the Earth's surface is rather peculiar. The distribution of the "usual" stable molecules has been sufficiently well investigated. On the other hand, the distribution of the unstable molecules and atoms, which are produced by photochemical reactions and solar radiation, is much less well investigated in this layer.

The dissociation of oxygen, which is very important for the energy balance in this layer of the atmosphere, apparently begins at 80-85 km. The D layer of the ionosphere, whose existence is probably linked with the NO molecules, is found at an altitude of about 60 km. Therefore, the investigation of the atmosphere at these relatively low altitudes is of considerable practical and theoretical interest.

Our knowledge of the composition of the atmosphere between 100 and 250 km is still quite inadequate: very few measurements have been made in this region, where the numbers of neutral and charged particles are approximately equal. We know slightly more about the ionic composition at a given height than about the corresponding distribution of neutral molecules. At present, we have only qualitative (or at best semiquantitative) data about the latter.

Little is known about the region above 250 km. Investigations at these altitudes are carried out by means of radio frequency mass spectrometers sent up from the Earth in artificial satellites. The first and so far the only investigations in this region have been carried out by the Soviet Union and concern the ionic composition of the outer atmosphere.

In those regions of the atmosphere in which both neutral and charged particles are found, we can expect that there will be both seasonal and daily variations, as well as latitudinal variations, in the composition. At present, however, we know practically nothing definite about this.

Finally, we shall explain why, in this book, we have divided the atmosphere into different layers. This can be seen from the chapter headings. The division is linked with the development of the subject, each layer corresponding to the use of a certain method of propulsion. Moreover, this division corresponds roughly to a division in the experimental methods used: each layer has its own methods of investigation, which are not normally used for any other layer.

Chapter I

INVESTIGATIONS OF THE LOWER ATMOSPHERE

Introduction

The study of the atmosphere can be traced back to classical times. This is hardly surprising since air, which surrounds man and is vitally necessary for his existence, could not avoid attracting his interest and attention. As an integral part of the universe, air interested the ancients (of China and India) and the Greek philosophers of the 5th and 4th Centuries B. C. It is therefore no accident that air was one of the four elements from which "all things were made" (earth, water, air and fire). These four elements, and the various ways in which they could be combined, formed the basis for the later Greek philosophers' view of the world. They also formed the basis of the famous "Chārvākas" system of philosophy in India (in the 5th Century B. C.). In Europe, thanks to Aristotle's incontestable authority, this concept of the "four elements" won general recognition, dominating the thought of nearly all later classical philosophers and mediaeval scholastics*

In the earliest period of Greek philosophy, one of these elements usually occupied a dominant position. For example, Thales (6th Century B. C.) suggested that water was the basic element, while Anaximenes (548-529 B.C.) gave the precedence to air. He said, "Everything comes from condensed or rarefied air: earth, water and fire, and from them other bodies; everything turns into air when it is decomposed. Air is indestructible and constantly in motion".

After Anaximenes, Diogenes Appolloniates (460 B. C.) "adopted Anaximenes' teaching that air is the primary substance. All creative work, all material actions are nothing but inhalation and exhalation. Man is superior to the animals because he breathes in purer air, since he does not bend his head down to the ground like they do" /1/.

Such a doctrine, a typical example of the metaphysical views of the classical philosophers, prevented them from obtaining a correct perception of the nature of the world. However, alongside such metaphysical concepts the Hindu and classical philosophy of the 5th Century B. C. also produced and developed the study of atomic materialism, which permitted a deep insight into the essential structure of matter. Thus, for example, according to the Hindu Uluk* (5th Century B. C., founder of the Vaiśeshika philosophy), the whole Universe is composed of four kinds of vanishingly small, indivisible particles: atoms of earth, water, air and light. Air, according to

* It is interesting to mention that in the very ancient Chinese philosophy of the 9th–7th Century B. C., air was not yet included among the "basic" elements.

** [Both the Encyclopedia Britannica and the Bol'shaya Sovetskaya Entsiklopediya give Kanada as the founder of the Vaiśeshika philosophy.]

Uluk, was an aggregate of a countless number of identical particles*.

According to the Creek philosophers Democritus (460–370 B. C.) and Epicurus (341–270 B. C.), air, like all substances, consists of separate, very small particles (atoms); but unlike Uluk the Greek philosophers assumed that the different atoms differed considerably in shape and were always in constant motion.

Of course, the abstract, contemplative reasoning of the ancient philosophers did not lead to much real knowledge about the atmosphere. Their scorn of any kind of experimental verification of observed facts could not help but limit their knowledge to such naive ideas. Even Aristotle, whose philosophy stimulated the thought of many succeeding generations, considered experiment a secondary affair which hardly merited the attention of a student of the philosophy of pure knowledge. However, the vital needs of humanity prevailed, turning "pure" philosophy more and more towards experiment. Aristotle himself compared the weights of inflated and uninflated bladders in order to demonstrate that air has weight: he found that the inflated bladders weighed more, and concluded that the air itself must weigh something**. Other properties of air (its pressure, mobility, compressibility, etc.) were elucidated at about the same time.

For the ancient thinkers, air was the only "airlike" substance there was. It differed sharply from all other substances on the Earth, it was absolutely uniform and indivisible, and it extended from the surface of the Earth to the ends of the Universe. Gases found in caves, produced by the decomposition of organic matter, from mineral springs, from erupting volcanoes, etc., were supposed to be merely tainted air, produced either by the addition of other substances or by an alteration of the physical properties of the normal "good" air (rarifaction, compression, decrease in mobility, etc.). Thus, for example, Lucretius (1st Century B. C.) described an Avernal place, above which birds were suffocated and fell to the ground***. He interpreted this phenomenon in a very materialistic manner: a poisonous substance emitted by the Earth must either have contaminated the air or rarified it. Consequently, the birds lost their support.

Lucretius, living just before the start of the Christian era, was the last brilliant exponent of the study of atomic materialism. The age of the medieval scholastics reduced this amazing philosophy to silence for a long time; after more than fifteen hundred years it was reawakened and voiced again. The profound thoughts of the ancient atomists about the nature of air were also silenced for a long time.

The dark times of the Christian middle ages had their own special kind of "Avernal" atmosphere, suffocating all life. The achievements of classical

* This fruitful idea of Uluk appears to have been unknown to Europeans, although Democritus, who was much traveled (and had in particular visited India) may have come across it there.

** The result of this experiment is rather questionable. As shown by Benedetti as early as the 16th Century, an inflated bladder should weigh just as much as an uninflated one, owing to the applicability of Archimedes' principle to the process of weighing in air. However, this is only true if the air in the bladders is not compressed. We must assume that in Aristotle's experiment the bladders were inflated as much as possible, giving an excess of air inside; moreover, even if the bladders were only weakly inflated, there would have been a slight excess pressure inside them, to overcome the elasticity of the bladders, and their weight. It is thus possible that Aristotle really did observe an increase of weight in the inflated bladders.

*** This place, Lake Avernus in Italy, owed its effect to the high concentration of sulfurous fumes emitted from the water. Lucretius described this and similar places in his poem "De rerum naturae" (Book 6).

science, and primarily the atheist study of Democritus, were mercilessly suppressed and purposefully condemned to complete oblivion, and it is only thanks to the Arabs that many works of the great thinkers of antiquity have been preserved.

After careful study, the Arabs enriched the ancient legacy with the results of their own science and with the knowledge they had gained of Indian and Chinese studies. In those times of scientific censure, the Arabs were worthy inheritors of the scientific tradition. It is not surprising, therefore, that we find here the next advance in the ideas on the nature of the air. The Arab scientists of the 8th Century A. D., particularly Jabir (Geber), formed the idea that different "air-like" substances might exist in nature. For example, we find Jabir making the following statement about chemically reactive gases: "Oh son of science," he says, "if you desire different kinds of knowledge about bodies, you can only achieve this aim with the aid of spirits (gases-author). When these spirits gain a foothold in a body, the latter loses its original form and nature: it no longer remains what it was. If you force the spirits to be released again, one of the following may happen: either the spirit flies away, leaving the body undisturbed, or both spirit and body disappear together" /1/. Jabir was also acquainted with the fact that metals gain weight when they are roasted in air (calcination)*. This fact, which was destined to play an important part in the development of modern chemistry and the overthrow of the phlogiston theory, was forgotten at this time and was not "rediscovered" by western scientists for about a thousand years (!), when it helped Lomonosov and Lavoisier to open the way to an understanding of the chemical properties of air.

In medieval Europe, science dragged on a pitiful existence, and the investigation of air aroused little interest. Matters changed radically when Leonardo da Vinci started his investigations, at the end of the 15th Century.

Some of the vast variety of subjects which Leonardo da Vinci studied were directly related to the investigation of air. With the perspicacity of genius, he stated that air "consists of many component parts"/2/, and this was about 300 years before the work of Lavoisier! Moreover, he had an excellent understanding of the significance of air in the processes of respiration and combustion. He know that only part of the air supported combustion, and that the other part was good neither for combustion nor for respiration. This may be seen from the following quotation from his manuscripts: "The element fire continuously devours air, part of which feeds it, and a vacuum tends to be formed if air is not added to fill it... Where a flame cannot burn, animals which breathe cannot live"/3/. Leonarado da Vinci's brilliant ideas left the science of his days so far behind that his contemporaries often completely failed to understand them. His ideas about combustion and the complex structure of air were forgotten and therefore remained undeveloped.

A century later, the Flemish chemist van Helmont (1577-1644) began to distinguish certain gaseous substances from air. "Van Helmont was the first to make a clear distinction between air and those air-like substances produced in combustion, fermentation, the action of oxygen on metals, etc.

* It is interesting to mention a few more achievements of Arabic science: Alhazen (11th Century) determined the height of the atmosphere by observations of the twilight, and came to the conclusion that it must exceed 52,000 paces (assuming the density of the air to be constant). Another Arabic scientist, Alhatsin (12th Century), was well aware that air had weight, and pointed out that Archimedes' principle, which determines the loss of weight of a body in a liquid, applied to air /4/.

He was the first to apply to them their present name – gases" /5/.

Thus, the study of air formed the basis for the science of gases in general. However, van Helmont did not consider air as a gas. He also distinguished between vapor, which can condense to liquid at low temperatures, and air, which cannot. At the start of the 17th Century, the ideas about air began to take definite form. Air was distinguished from the following other types of gaseous substances: "gas silvestre" (what we now call carbon dioxide) and "gases from fat", produced by the combustion of organic matter. But unfortunately, van Helmont's ideas met the same fate as Leonardo da Vinci's; they were not understood by his contemporaries and were soon forgotten. For a long time the term "gas" was little used; finally, it was introduced into current use by Lavoisier (1777).

Despite the unfortunate neglect of van Helmont's work, experimental investigation of air and "air-like" substances was continued and developed. In 1670, Boyle collected gases in special vessels. Unlike van Helmont, he called these new gases "artificial air", which we may regard as a retrograde step. In 1755, Black thoroughly investigated carbon dioxide, but he too was unable to get out of the established habit of using a cumbersome nomenclature: he called carbon dioxide "fixed air", even though it is completely different from normal air. After Black, Mayow (1643-1678) and Hales (1677-1761) made the next important advance in the technique of handling gases: they collected gases in inverted vessels above water. Hales collected samples of gases in what he called a "pneumatic trough", which was probably the first piece of "apparatus" used for studying gases. However, the first serious attack on the problems of air was made in the 1770's, by Cavendish (1731-1810), Priestley (1733-1804) and Scheele (1742-1786). These three scientists, who were all ardent adherents of the phlogiston theory, made highly important experimental discoveries at practically the same time (in connection with the discovery of oxygen and nitrogen in air), but they did not draw the right conclusions from their discoveries. In order to give a better understanding of the development of the investigations about this time, we must say a few words about the phlogiston theory and its significance in the development of the science of gases, in particular, air.

By the beginning of the 17th Century, a large number of unconnected facts, which were difficult to arrange in any meaningful pattern, had been accumulated by experimental chemistry and physics. Among the attempts to explain these facts was the phlogiston theory, put forward by Stahl (1660-1734). Phlogiston was a substance with a negative weight and was present in all bodies, thus decreasing their weight. When a body burnt, it lost phlogiston. The phenomenon of metal calcination was regarded as a direct confirmation of this theory. It was supposed that metals consisted of "calx" and phlogiston; when the metal burned, phlogiston was evolved, the calx which was left being heavier than the original metal. A burning body, in other words, decomposed into phlogiston and residue. "This theory quickly gained wide acceptance, which is not surprising: Stahl had succeeded where even Newton had failed – in offering one general explanation for as many disparate chemical phenomena as possible. This was the first chemical theory to take a sufficiently large number of facts into account, and to give a comprehensive explanation for them" /5/. The first crushing blow to the phlogiston theory was delivered by the work of M. V. Lomonosov, who studied the calcination of metals in detail and came to the conclusion that the reason

for the increase in the weight of metals during calcination is not that they lost phlogiston but that they take up particles of air. Lomonosov wrote, "I carried out the experiments in sealed glass tubes, to see whether the weight of metals was increased by heating alone. These experiments have shown that the famous Robert Boyle is wrong in his opinion, for unless air is admitted from outside, the weight of the burning metal remains constant" /6/. Further, in a letter to Euler (1747), Lomonosov stated: "There is no doubt at all that particles of the air flowing continuously over a burning body combine with it and increase its weight". However, despite such definite proofs of the error of the phlogiston theory, enthusiasm for it was so great that it continued to reign undisturbed over the minds of scientists for about a century. In 1774 Priestley, who had prepared oxygen and was investigating it, came to the conclusion that air contained phlogiston, and that the gas he had made was "dephlogisticated air". About the same time, the Swedish chemist Scheele came to the conclusion that air consisted of two elastic fluids: "fire air" (oxygen) and "foul air" (nitrogen). Scheele carried out his analyses with the aid of substances which absorbed part of the air, such as "nitrous air" [NO], moist iron fillings, etc. These substances absorbed about 1/5–1/3 of the air; the residue would not support combustion. This residue was investigated as long ago as 1772 by Cavendish, a man with an amazing gift for experimental method. He called this gas "azote", but did not publish his work. Therefore the discovery of nitrogen is credited to D. Rutherford, who published his work on this problem in 1772.

Thus, after a long and tortuous quest, it was finally shown that air consists of two components (two airs, as they said in those days): "dephlogisticated air" (without phlogiston) and air containing phlogiston (nitrogen). But the correct interpretation of these last discoveries was left to Lavoisier (1743-1794). Finally, rejecting the phlogiston theory, Lavoisier checked the results of previous investigations by means of accurate experiments, and became convinced that air contains two gases, which he named "vital air" (oxygen, the modern name referring to its ability to produce acids) and "azote" (nitrogen, not supporting life). He also showed that when metals are calcined, the oxygen of the air combines with the metal to give a scale (the metal is oxidized), this process being accompanied by an increase in weight. Thus, the fact which was already known to the Arabs (Jabir) was finally explained in full.

Therefore, the fact which seems so simple and obvious to us, that air consists mainly of two gases (oxygen and nitrogen), achieved its place in science after the work of many generations of scientists. This work was crowned by the creation of a new science of gases and the complete destruction of the phlogiston theory.

1. Early geophysical investigations

The history of the investigation of air during the next hundred years (1790-1890) is concerned with somewhat different problems from those investigated earlier.

The basic components of air (oxygen, nitrogen, carbon dioxide and water vapor) having been discovered and investigated, the problem of the chemical composition of the air was regarded as being more or less solved. There only remained the question: is air a mixture of gases or a chemical

compound. This question divided the investigators into two groups; those (not very many, it is true) who held air to be a chemical compound of the type N_4O /7/, and those, (the much larger group) who regarded it as a mechanical mixture of these gases. Even Lavoisier and Dalton were not sure which side to take in this matter /8/. However, discoveries were very quickly made which left no doubt as to the correctness of the second point of view. Thus, it was shown that oxygen and nitrogen are miscible in all proportions without any heat being produced or absorbed. This immediately showed that there is no chemical reaction between these gases. Moreover, the total volume of the mixture thus obtained was always exactly equal to the sum of the volumes of the original gases. These and many other facts soon made it obviously clear that air is indeed a mechanical mixture of its component gases.

After solving this problem, the investigators found themselves faced with problems of a geophysical nature: the constancy of the air composition at different places on the Earth's surface and at different altitudes, the effect of the weather on the air composition, etc.

Solving these problems was no less difficult than solving the problem of the chemical composition of the air. It was necessary in the first place to have sufficiently accurate equipment for determining the chemical composition of the air, and in the second place to carry out experiments on a "world-wide scale". Both of these tasks were carried out in the period 1790-1890, thanks to which it was possible to answer these questions, if not completely, at least to a very considerable extent.

Originally, as we now know, people had false ideas about the composition of the air. They thought that the ratio of nitrogen to oxygen in the air was subject to fluctuations, and depended strongly not only on the geographical location of the spot where the air sample was taken but also on the weather conditions there at the time. Such ideas were "confirmed" by experimental results obtained with very primitive analytical equipment. Overestimating the accuracy of their analyses, and not taking into account the imperfections of their investigation methods, investigators formed erroneous conclusions about the variability of the oxygen content of the air. If we consider the kind of equipment used by the investigators in those days, it is no wonder that they obtained contradictory results. We have already mentioned the first "apparatus", if it can be given this name, namely Hales' "pneumatic trough", which consisted of a large vessel completely full of water; in this vessel a number of inverted glass containers were placed for collecting gases. These gases were led through the water by means of bent glass tubes to the containers. It was naturally difficult to obtain anything but qualitative or crude quantitative results with such equipment.

The invention (by Priestley and Hales) at the end of the 18th Century of the "eudiometer" (a word of Greek derivation, meaning "a device for measuring fair weather"), was a great step forward. Originally, this was simply a vessel in the pneumatic trough, with graduations marked on it so that the change in volume of the gas in it could be measured after a chemical reaction.

In order to determine the oxygen content of an air sample contained in this eudiometer, a substance which consumed the oxygen was introduced, and the percentage of oxygen in the air could then be calculated from the decrease in volume of the gas.

For example, methods using phosphorus (Berthollet, Parrot), an alkaline solution of pyrogallol ($C_6H_3(OH)_3$), ferrous sulphide, etc., were widely used

for absorbing the oxygen. But the method which achieved most popularity with investigators was that of allowing the oxygen ("dephlogisticated air") of the air in the eudiometer to react with nitric oxide ("nitrous air"). This reaction produces brown fumes of nitrogen dioxide, which can easily be removed by absorption with alkali. The percentage of oxygen removed from the air sample in the eudiometer can then simply be calculated from the reduction in volume.

These simple methods, allowing the composition of the air to be determined in a very straightforward way, attracted the attention of a wide circle of investigators. The literature of that time contained many reports of investigations on the composition of air, with widely differing results. This is hardly surprising, since each investigator used his own method for calculating the decrease in the volume of gas in the eudiometer, while the reagents used were often not very pure. However, as E. A. Paneth /9/ quite rightly remarked, if we consider the methods used in those days for investigating the composition of the air, we should not be surprised at the many erroneous results. On the contrary, we should admire the way they managed to obtain such concordant and accurate results with such poor means at their disposal.

The work of Cavendish (1783-1784), who used a nitric oxide eudiometer to determine the oxygen content of air, stands out from among the many investigations of his contemporaries. "Cavendish showed that the ratio of the two main component gases of air was remarkable constant. The accuracy of these analyses, and especially of those published in the following year, is remarkable: all the values for the content of "dephlogisticated air" oscillate about 20.84%" /5/. In order to appreciate fully the really outstanding results of Cavendish's accurate experimental work, we should remember that the present-day figure for the oxygen content of air, obtained with accurate equipment, is 20.95%.

Having decided in his own mind that the composition of the air was constant, Cavendish subjected the existing works on the determination of oxygen in air to a careful scrutiny and serious scientific criticism. He showed that the differences between the results of the various investigators were the result of experimental errors and inaccuracies, of which he described about twenty (!).

More reliable investigations of air did not however begin until Volta invented the electrical eudiometer* (Figure 1). Volta made use of the fact, known at that time, that the passage of an electric current (spark) through a mixture of "inflammable air" (hydrogen) and normal air caused an explosion, as a result of which dew was formed on the walls of the vessel containing the mixture of gases. The eudiometer was operated as follows. The air and a roughly equal amount of hydrogen were introduced into the vessel and the total volume of the mixture was determined. The mixture was exploded by means of an electric spark. The volume of the mixture was redetermined, and the decrease in volume calculated (the volume of the dew on the walls being ignored). Knowing that water is formed from one part of oxygen and two parts of hydrogen, we may conclude that one third of the

* B. N. Menshutkin attributes the invention of this eudiometer to Cavendish.

decrease in volume of the gaseous mixture is due to the disappearance of oxygen from the air*.

In his work "Concerning a New Eudiometer", which appeared in 1783, Cavendish described the improved eudiometer which he had designed.

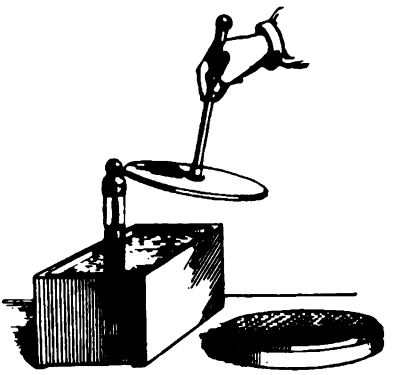


FIGURE 1. Volta's eudiometer

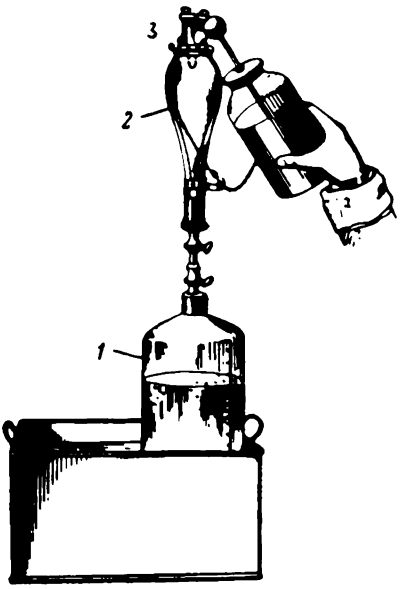


FIGURE 2. Cavendish's eudiometer

The graduated vessel 1 is placed in the tank filled with water, as shown in Figure 2. The air under investigation is introduced into this vessel, together with hydrogen. The thick-walled vessel 2, which has a tap and two platinum wires sealed into its upper part, is then screwed on to the top of 1. Initially, vessel 2 is evacuated. When the connecting taps are opened, the mixture of gases flows into vessel 2, after which the water level in the lower vessel is carefully recorded. The taps are then closed again, and the mixture in the eudiometer is exploded by the passage of a spark between the two platinum wires. When the taps are opened again, the level of the water in the graduated vessel rises, and the new level is also recorded.

By reasoning similar to that indicated above, the oxygen content of the air under investigation can be calculated from the difference between the two levels. Gay-Lussac found this the best apparatus to use for his investigations of the chemical composition of air. However, for the measurements made with this eudiometer to be completely reliable, it was necessary to check the assumption that detonating the mixture causes one volume of oxygen to react with two volumes of hydrogen. The experiments of Gay-Lussac and Humboldt, carried out with extreme accuracy, unequivocably established

* It was already known at that time that the "dew" on the walls of the eudiometer was water. Cavendish and Priestley (1783) established that the weight of the drops of water was equal to the sum of the weights of the reacting gases, and Watt, analyzing their results, showed that water consists of hydrogen and oxygen. The fact that water consists of exactly one part of oxygen and two parts of hydrogen was however not known until later.

the accuracy of this assumption, thus allowing Cavendish's eudiometer to be used for accurate work.

Round about 1806, Gay-Lussac and Humboldt made a large number of analyses of the air in various countries during their travels together. These analyses, carried out using the Cavendish eudiometer, showed (in contrast to previous investigations) that the composition of the air was completely constant. This work of Gay-Lussac and Humboldt was the first "world-wide" experiment of a geophysical nature.

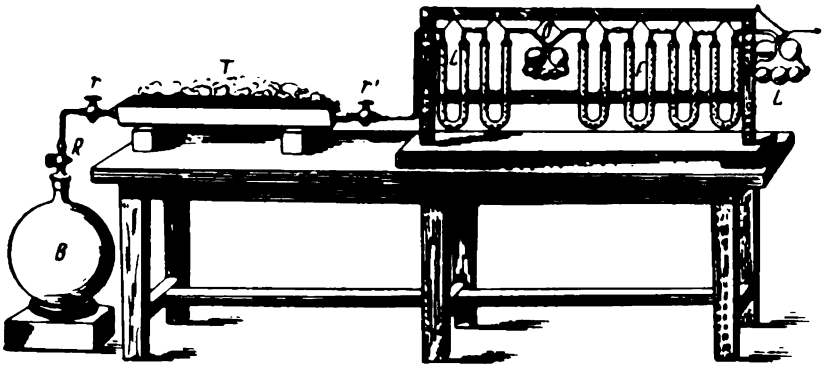


FIGURE 3. The apparatus of Dumas and Boussingault for the gravimetric analysis of atmospheric air

In 1841, Dumas and Boussingault succeeded for the first time in weighing the oxygen and nitrogen in a given volume of air. The weighing method is, as is known, much more accurate than the method of measuring volumes (eudiometer). Therefore the accuracy of the analyses of air is considerably increased by use of the method of Dumas and Boussingault. Moreover, this method allows both the main constituents of air (oxygen and nitrogen) to be determined, and not just oxygen alone, as was the case previously (in the eudiometer). The principle of the weighing method consists in passing air over red-hot copper, which removes all the oxygen. The increase in weight of the copper gives the amount of oxygen in the air, while the remaining gas (nitrogen) is determined by direct weighing.

The apparatus of Dumas and Boussingault is shown in Figure 3. The glass bulb B of volume 10–15 liters is connected via the tap R to the heat-resistant glass tube T. This tube, which is packed with copper filings, is provided with taps r and r' at its two ends; via the tap r' it is connected to the group of U-tubes t, packed with pumice covered with sulphuric acid. These are followed by Liebig bulbs O filled with sulphuric acid, more U-tubes filled with pieces of potash, and finally more Liebig bulbs L filled with a solution of potassium hydroxide. The open end of the tube leads out of the room. The analysis is carried out as follows: the bulb B and the tube (with copper) are first evacuated separately and weighed, and then connected up again as shown in the figure (being kept as well evacuated as possible in the process). The tube T is then heated over a coal fire until the copper filings are red hot. Tap r' is then opened, then tap r, and finally (slowly) tap R. Air enters the "empty" bulb B, passing first through the whole analytical system. The bulbs L and the U-tubes f remove carbon dioxide, which is absorbed by the potassium hydroxide, while the bulbs O and U-tubes

t remove water vapor, which is absorbed by the sulfuric acid. On passing over the red-hot copper, the air oxidizes the latter, thus getting rid of all its oxygen, so that only "pure" nitrogen reaches the bulb B. When air ceases to enter the apparatus, the taps r', r and R are closed again, the copper is allowed to cool, and B and T are reweighed. The increase in weight of the tube T with its copper filings is a direct indication of the amount of oxygen taken up, while the increase in weight of the bulb B similarly gives the amount of nitrogen. In this way, Dumas and Boussingault found that air contains 20.8% oxygen and 79.2% nitrogen. This is not far from the truth. The same apparatus can also be used to determine the amount of carbon dioxide and water vapor in the air: in fact, if the tubes containing sulfuric acid are weighed before and after the air passes through, then the difference in weight gives the amount of water vapor in the air which was absorbed by the sulfuric acid. This is still considered to be the most accurate method of measuring moisture content /10/.

Similarly, the amount of carbon dioxide gas absorbed by the potassium hydroxide can be found by weighing the tubes containing the alkali.

Another method for determining the carbon dioxide in the air was suggested in 1880 by the chemist Moore /11/. This method is also based on the absorption of the carbon dioxide by alkali (potassium hydroxide), but the amount absorbed is measured in a different way. The air is drawn in succession through three bulbs joined together by glass tubing and containing a solution of potassium hydroxide (KOH). The carbon dioxide in the air reacts with the KOH, forming potassium carbonate in the water. The air is drawn through the system for 24 hours and its volume measured by a special meter. All the carbon dioxide remains in these three vessels (the last one contains only traces). The determination of the carbon dioxide is then

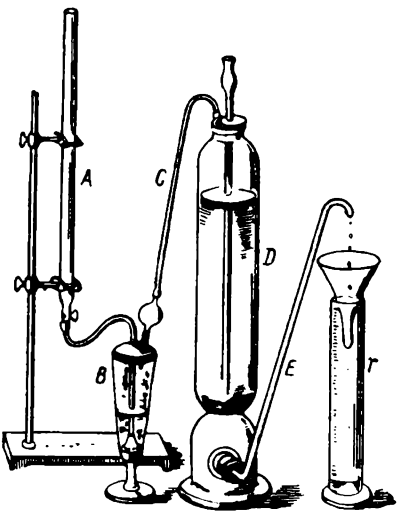


FIGURE 4. Moore's apparatus for measuring the carbon dioxide content of atmospheric air

carried out in the apparatus shown in Figure 4. The vessel B, containing the carbon dioxide, is connected to the burette A and the cylinder D as shown

in Figure 4. The cylinder D contains water, and has an outlet tube at the bottom which is bent in a swan-neck so that its top is just at the level of the water. Therefore, the water cannot run out of D. The burette A is now filled with a 50% solution of hydrochloric acid and its tap opened. The acid, flowing into B, reacts with the potassium carbonate to give potassium chloride, water and carbon dioxide. The latter rises through the tube C and displaces water into the measuring cylinder. The carbon dioxide is prevented from dissolving in the water in D by a layer of petroleum floating on the surface of the water.

In the 1840's, Müntz and Oben suggested a simple "field" method for determining carbon dioxide. They used sealed, well evacuated glass tubes filled with potassium hydroxide. On the spot where the sample is to be taken, such a tube is opened and a known amount of air pumped through it. The tube is then sealed and sent for analysis. A sample taken in this way can be kept for a very long time (years).

Our description of the methods of analysis of air used by investigators in the middle of the 19th Century is now complete. We have seen that these methods are accurate enough to provide (at least to a first approximation) a solution to the geophysical problems we have mentioned above. And indeed, the middle of the 19th Century saw the beginning of an extensive and reasonably reliable investigation of the atmosphere.

Accurate investigations were made on the composition of the air at various points on the Earth's surface. "Gravimetric analyses of the air carried out by Dumas and Boussingault in Paris, under various weather conditions, from 27 April–22 September 1841 showed that the oxygen content only varied from 22.89–23.08% by weight, the mean value being 23.07%*. Brunner in Berlin, Bravais on the Faulhorn (in the Berner Oberland) at an altitude of two kilometers, Marignac in Geneva, Levi in Copenhagen and Stas in Brussels analyzed the air at the same time (and by the same method), and found that its composition did not exceed the limits of the composition found in Paris" /12/. The first Russian analyses of the air were carried out in 1829 by A. N. Kupfer, professor at the University of Kazan, who found an oxygen content of 21.0–21.2%.

We have already mentioned the first "world-wide" experiment of Gay-Lussac and Humboldt in 1806. The second such experiment was the work of Reynolds, who also decided to check the oxygen content of the air at various places on the Earth's surface, using more accurate equipment /118/. Scientists from different countries sent him air samples. The results of the analysis of these samples are shown in Table 1.

TABLE 1

Source of sample	O_2, %	Source of sample	O_2, %
Montpelier (USA)	20.95 ± 0.00	Mediterranean Sea	20.94 ± 0.01
Lyon	20.94 ± 0.01	Atlantic Ocean	20.94 ± 0.01
Normandy	20.95	Arctic Ocean	20.91 ± 0.01
Berlin	20.96 ± 0.01	Paris	20.96 ± 0.01

These results led Reynolds to the conclusion that the oxygen content of the air is constant over the whole globe, with a value of 20.94%. Levi

* The extreme values correspond to 20.68 and 20.88% by volume, and the mean to 20.87% by volume.

obtained very similar results in 1841, after measuring the oxygen content of the air in Paris (21.01 %), the Atlantic Ocean (20.95 %) and South America (21.02 %). Many other observations gave a mean value of 21 %. Thus, in the middle of the 19th Century the problem of the composition of the Earth's atmosphere was solved, to a first approximation: it was shown to be constant everywhere — 21 % oxygen and 79 % nitrogen.

Does the oxygen content of the air depend on the time of day or the season of the year? This was the next problem, which was also more or less solved by the investigations of Levi, Dumas and Boussingault. It was shown that the oxygen content of the air does not depend on the season, but is (very slightly) greater in the day time than at night. Thus, Martins and Bravais found the figure at night to be 20.68 %, and in the day 20.74%; Levi, in the Atlantic Ocean, found: night 20.96 %, day 21.06 %.

The idea that the oxygen content of the air depended on the weather was very widespread at this time. This idea was based on the fact that it had been suggested in the time of Dalton that air at high altitudes differed in composition from air near the Earth's surface, the upper air being enriched in the lighter gas (nitrogen). Thus in a cyclone, in which there is a rising current of air, the oxygen content should be relatively high; while an anticyclone, with its descending current of air, should give relatively more nitrogen. Jolly in Munich (1880) and Merley /13/ even claimed to have observed such an effect, but later, more accurate investigations showed such claims to be groundless.

A particularly accurate investigation of this problem was made by Kreusler /14/, who made an extensive series of observations in Bonn in 1885, and showed that the oxygen content of the air does not depend on metereological conditions.

In 1912, Benedict /15/ confirmed all Kreusler's experimental results, stating in conclusion that "air is a physical mixture of constant chemical composition"; and in 1919 Krogh /16/ stated that the percentage content of nitrogen in the atmosphere is a geophysical constant which can be determined to a high degree of accuracy.

TABLE 2

Investigator	CO_2, %	Investigator	CO_2, %
Scheele (1782)	6	Thénard (1812)	0.04
Priestley (1783)	2	Boussingault (1840)	0.04
Gartner (1801)	1	Risler (1872)	0.03
Humboldt (1804)	1	Levi (in Montsûrs) (1875)	0.03
Parrot (1804)	0.5	Müntz and Oben (1882)	0.028
Dalton (1805)	0.068	Modern data	0.03–0.027

At the same time as these oxygen-nitrogen investigations of the atmosphere, investigations into its carbon dioxide (CO_2) content were also being carried out. As we have already seen, carbon dioxide ("forest gas") was discovered by van Helmont in 1674. However, it was not for another century (1774) that the presence of CO_2 in the atmosphere was discovered, by Bergman. Both van Helmont and Bergman thought that it was an element, and Lavoisier was the first to determine its composition accurately.

Different investigators found different values for the amount of carbon dioxide in air; it is striking that as more accurate methods of determination were devised, the measured carbon dioxide concentration content of the

atmosphere fell. To illustrate this, Table 2 shows some data already published by Rykachev /11/ together with some data collected by ourselves.

Produced by the respiration of living organisms, by the fermentation of organic substances, by the eruption of volcanoes, carbon dioxide might well be expected to be present in the atmosphere in widely differing concentrations in different parts of the Earth and at different times of the day and year. But in fact the concentration of carbon dioxide in the atmosphere has been shown to be remarkably constant. Rykachev /11/ gives the following data on the CO_2 content in 10^{-2} % during each month of the year (according to analyses in Montsûrs):

January	3.03	July	3.01
February	3.03	August	2.96
March	2.99	September	2.99
April	3.00	October	2.93
May	3.00	November	2.93
June	3.07	December	2.93

The mean of 2500 values measured throughout the year was $3.00 \cdot 10^{-2}$ %. Similar results were found by Reise (in Dienne): $2.942-2.978 \cdot 10^{-2}$ %, Boussingault and Levi (in Paris): $3.190 \cdot 10^{-2}$ %, Andaln (in Alsace): $2.989 \cdot 10^{-2}$ %, and others. These investigators found a very slight daily fluctuation in the CO_2 content, as shown in Table 3.

TABLE 3

Investigator	CO_2 content, 10^{-2} %	
	day	night
Boussingault and Levi	3.9	4.2
Reise	lower	higher
Trochu (in town)	3.53	4.03
Trochu (in country)	3.14	3.78
Müntz and Oben (in country)	2.70	
	2.79	about 3.00

This great constancy of the CO_2 content may be attributed first to very thorough mixing of the atmosphere, and second, as pointed out by D. I. Mendeleev, to the fact that "the water of the oceans contains CO_2 in solution, and thus acts as a huge reservoir, regulating the amount of this gas in the atmosphere. Thus, when the partial pressure of carbon dioxide in the air falls, this gas is replenished from the sea, and if the partial pressure rises it dissolves in the sea. In this respect, as in so many others, nature is in a state of dynamic equilibrium" /12/*.

A number of other compounds were discovered in the atmosphere at the end of the 19th Century. These were present in even smaller quantities than CO_2, and their concentration varied quite considerably with the time and the place of investigation.

Cavendish knew that when a spark passed through air, the nitrogen reacted with the oxygen giving nitrogen compounds (nitrogen dioxide, and in the presence of water vapor also nitric acid). Now similar conditions are quite common in the atmosphere: thunderstorms and silent electric discharges occur everywhere. It is hardly surprising, therefore, that the search for

* Recently, results have been published which indicate that there has been a certain increase in the CO_2 content during recent decades; but this work still needs careful checking.

various oxides of nitrogen was successful. Ammonia was also found (Chabroux, Thénard), as well as nitric acid and ammonium nitrate. Hydrogen peroxide was discovered in air by the Moscow Professor Shene in 1874, and methane by Boussingault and Verve. Very small concentrations of iodine were found, and also ethyl alcohol (Müntz).

Summing up the investigations of the atmosphere in this period (1790-1890), we may say that nearly all the geophysical problems posed were solved with such accuracy that the results obtained are still valid today. By the end of the 19th Century, the chemical composition of the atmosphere was recognized to be constant (Table 4).

TABLE 4

Gas	% by volume
Nitrogen	79.10
Oxygen	20.87
Carbon dioxide	0.03

Finally, we must mention a very important discovery made by Schönbein in 1840 /142/. He detected ozone in the atmosphere; this compound is produced by the passage of a silent electric discharge (glow discharge) through the air. He also showed how the ozone in the atmosphere could be investigated very simply with the aid of "ozonometric paper", which is simply strips of normal paper soaked in a solution of potassium iodide and starch. When exposed to the air, this paper becomes more or less strongly blue, depending on the ozone content of the air. Further investigations of atmospheric ozone used much more refined methods (optical methods, special methods of chemical analysis, etc.). The investigation of ozone in the atmosphere has developed into a study in itself.

2. The discovery of new gases in air; the present state of knowledge of the gaseous composition of the lower atmosphere

The third period of the investigation of the lower atmosphere was initiated by the unexpected discovery, by Rayleigh and Ramsay in 1894, of new permanent gaseous constituents of air. In 1892, Rayleigh, who had prepared nitrogen in two different ways — from air and from nitrites — found that a liter of nitrogen obtained from the air was always very slightly heavier than a liter of nitrogen produced by chemical means. Ramsay suggested that this was due to the presence of an unknown, relatively dense gas in air. This was a daring, not to say risky suggestion, considering the thoroughness with which the composition of air had been investigated. Rayleigh and Ramsay collaborated to show that this was in fact the case. Ramsay removed the nitrogen and oxygen from the air by chemical means, thus producing traces of the new gas. The same gas was prepared by Rayleigh, who removed the oxygen from the air by Cavendish's method (see above).

"Rayleigh and Ramsay reported this discovery to the meeting of the British Association in Oxford, in August 1894. Their announcement was initially greeted with complete disbelief: it was inconceivable that such an

enormous fraction of the air — a whole percent — should have escaped the attention of vigilant chemists for a whole century. Everyone rushed to check the experiments of Rayleigh and Ramsay, and found that they were right, that air really did contain "argon"*, as the new gas was called" /5/.

The complete inertness of the new gas to all chemical reagents explained why 1 % of this gas had remained unnoticed in air, while minute amounts of such gases as CO_2, O_3, HNO_3, etc. (hundredths or thousandths of a percent) had already been thoroughly investigated. The discovery of argon was so unexpected that there was initially not even a place for it in Mendeleev's periodic table. Mendeleev himself originally thought that it was a stable compound of nitrogen of the formula N_3. But it was soon shown that argon was a monatomic gas of atomic weight 40. Later, as is well known, Mendeleev created a "zero" group in his periodic table specially for argon, the remaining places in this group being filled by the other inert gases. This once again confirmed the brilliance of this Russian chemist's discovery of the periodic law.

The discovery of argon immediately suggested the possibility of there being other unknown gases in air. Energetic investigations in this direction were completely successful: other inert gases were discovered in air, though in such small quantities that they could hardly be estimated.

The discovery of these gases was made possible by the invention of a method of liquefying air in large quantities. In 1898-1899, Ramsay and Travers after evaporating some liquid air which they had produced, and also using spectral analysis, detected four new gases (helium, neon, krypton and xenon) in the residue. This showed that these gases are a composite part of the atmosphere. As a result of these new discoveries, the composition of air as known in 1906 was as shown in Table 5 /12/.

TABLE 5

Gas	% by volume
Oxygen	20.81
Nitrogen	78.23
Argon (and other inert gases)	0.90
Carbon dioxide	0.03
Other gases*	0.03

* "Other gases" includes atmospheric impurities, combustion products, dust, water vapor, and also such substances as ammonia, hydrogen, etc.

The discovery of these new gases at the end of the 19th Century aroused new interest in the problem of the composition of the Earth's atmosphere, which had seemed to be solved long ago. The efforts of 20th-century chemists and physicists was once more directed towards still more accurate determinations of this composition. The extreme accuracy which is demanded in this work can be understood when we realize that some of the inert gases in the atmosphere are present in concentrations of hundredths or even millionths of a percent. The difficulty of the task was accentuated by the fact that the inertness of the newly discovered gases made it impossible to use normal chemical methods for their determination, while physico-chemical methods of investigation were only just being developed.

* Argon–from the Greek meaning "lazy".

As we have already mentioned, the concentration of argon in air was determined by Ramsay and Rayleigh in 1894. Later work improved the accuracy of their value. Determination of argon was carried out by determining the nitrogen in the air and then separating off the argon. Thus, in 1906 Krogh /16/ found the concentration of nitrogen + argon to be 79.0215 ± ± 0.003 %. Separating these two gases by reacting the nitrogen with barium, Moissan /17/ found the following accurate values in 1903: N_2 78.09 %, A 0.93 ± 0.01 %, the latter figure including the other rare gases. Sufficiently accurate values were also obtained for neon and helium.

The first analyses of He and Ne were carried out by Ramsay in 1905-1908, and gave about $4 \cdot 10^{-4}$ % for He and $12.3 \cdot 10^{-4}$ % for Ne. The results of investigations of the concentration of these gases in atmospheric air are given in Table 6, taken from Glückauf's work /18/. At present, the figures in the last row of this table are used, i. e., Ne = $1.821 \cdot 10^{-3}$ %, He = $5.239 \cdot$ $\cdot 10^{-4}$ % (by volume).

TABLE 6

Investigator	He · 10^4 %	Ne · 10^4 %
Ramsay (1905)	4.0	12.3
Claude (1909)	5.0	15.0
Watson (1910)	5.4	18.2
Paneth, Glückauf (1936)	5.27 ± 0.05	-
Glückauf (1944)	5.24 ± 0.03	-
Paneth, Glückauf (1946)	5.239 ± 0.005	18.21 ± 0.04

While even the first analyses of He and Ne (Ramsay) were quite accurate, a considerable variation was found in early determinations of krypton and xenon in air, as may be seen from Table 7.

TABLE 7

Investigator	Kr, %	Xe, %
Ramsay, Travers /19/ (1889)	$1 \cdot 10^{-4}$	$5 \cdot 10^{-5}$
Ramsay /19/ (1903)	$5 \cdot 10^{-6}$	$6 \cdot 10^{-7}$
Ramsay /20/ (1908)	$2.8 \cdot 10^{-2}$	$5 \cdot 10^{-3}$
Moureu and Lepape /21/ (1926)	$(1.0 \pm 0.1) \cdot 10^{-4}$	$(0.9 \pm 0.1) \cdot 10^{-5}$
Damkölher /22/ (1935)	$(1.08 \pm 0.10) \cdot 10^{-4}$	$(0.8 \pm 0.1) \cdot 10^{-5}$
Glückauf, Kitt /118/ (1951)	$(1.14 \pm 0.01) \cdot 10^{-4}$	$(0.87 \pm 0.01) \cdot 10^{-5}$

At present, the last figures in this table are used. The analyses of recent years are remarkable for their high accuracy.

The determination of the hydrogen in the atmosphere has proved to be very difficult. Not only are the concentrations involved very small, but considerable error may be caused by traces of water in the sample; this water is easily decomposed to give hydrogen, and some workers have failed to correct for this. These traces of water are very difficult to remove, even with modern high-vacuum techniques. The walls of glassware which

is subjected to high vacuum continually emit traces of water vapor, which in such accurate experiments can completely mask the true analytical results. For this reason, determinations of the hydrogen content of the air are still subject to considerable variations today. Thus works round about 1900 gave figures which were much too high, of the order of 0.01 %. In 1902, Dewar /23/ found $1 \cdot 10^{-3}$ %, in 1909 Claude /24/ gave $1 \cdot 10^{-4}$ %, while in 1914 Dewar reduced the figure yet again, finding a value of $8 \cdot 10^{-5}$ % for the hydrogen content of the atmosphere; but even this value was too high. The most probable value is put at $5 \cdot 10^{-5}$ % /33/.

Apart from the above-mentioned gases, dry air always contains ozone and radon (radium emanation). According to the most recent data, the atmosphere normally contains 10^{-6} % ozone, the concentration increasing with height. The concentration of radon (a product of the disintegration of radioactive elements in the Earth's crust) is minute, even compared to that of the inert gases in the atmosphere ($6 \cdot 10^{-18}$ %). The determination of this very low concentration of radon was made possible thanks to the existence of extremely accurate equipment for measuring radioactive substances. The concentration of radon falls off rapidly with height. This is because the very short half-life of radium does not allow the element to rise far above the Earth's surface.

TABLE 8

% by volume									
N_2	O_2	A	CO_2	Ne	He	Kr	Xe	H_2	Reference, year
78.06	21.0	0.94	–	–	$4 \cdot 10^{-4}$	–	–	$3 \cdot 10^{-5}$	/25/, 1938
78.03	20.99	0.94	–	$1.2 \cdot 10^{-3}$	$4 \cdot 10^{-4}$	–	–	0.01	/26/, 1938
78.1	20.9	0.93	–	–	$5 \cdot 10^{-4}$	–	–	$3.3 \cdot 10^{-3}$	/27/, 1948
78.05	21.0	0.95	0.3–0.03	$1.2 \cdot 10^{-3}$	$4 \cdot 10^{-4}$	$5 \cdot 10^{-6}$	$5.9 \cdot 10^{-7}$	–	/28/, 1949
78.03	20.99	0.94	0.03	$1.2 \cdot 10^{-3}$	$4 \cdot 10^{-4}$	$5 \cdot 10^{-7}$	$5 \cdot 10^{-9}$	0.01	/72/, 1949
78.23	20.81	0.90	0.03	–	–	–	–	–	/29/, 1952
78.08	20.95	0.93	0.03	$1.8 \cdot 10^{-3}$	$5 \cdot 10^{-4}$	$1 \cdot 10^{-4}$	$1 \cdot 10^{-5}$	$1 \cdot 10^{-3}$	/30/, 1952
–	–	0.932	–	$1.6 \cdot 10^{-3}$	$4.6 \cdot 10^{-4}$	$1 \cdot 10^{-4}$	$8 \cdot 10^{-6}$	–	/31/, 1952
–	–	–	–	–	–	$5 \cdot 10^{-6}$	$6 \cdot 10^{-7}$		
78.08	20.95	0.93	0.03	$1.8 \cdot 10^{-3}$	$5 \cdot 10^{-4}$	$1 \cdot 10^{-5}$	$8 \cdot 10^{-6}$	$5 \cdot 10^{-5}$	/32/, 1954

The experimental results given here include some results which are not widely known. Many authors of textbooks and handbooks therefore quote values for the composition of the lower atmosphere which are either obsolete or sometimes even known to be incorrect. This situation is illustrated in Table 8.

At present, we may divide the gases which make up the lower atmosphere into two groups: those whose concentration is constant, and those whose concentration is variable. The first group, which makes up practically 100 % of the atmosphere near the Earth's surface, may be called "air"; the second, which is only a small fraction of the first, constitutes the "impurities". Water is a little difficult to place; it occurs in the air in the form

of water vapor, and can be present in quite considerable concentrations (up to 2-3 % by volume). Nevertheless, we have decided to place it in the second group, that of the impurities, at the same time qualifying the first group as the constituents of "dry air". We have also placed ozone in the second group. This substance, which is present in large amounts only at considerable altitudes, is a typical "impurity" in the lower atmosphere, its concentration varying considerably both in time and space.

Tables 9 and 10 give the most reliable values for the concentrations of the various constituents of the air near the Earth, and its impurities, based on modern work (see references /18, 22, 33, 118/). Despite the fact that these figures have been determined with the aid of the most modern equipment, they are not yet reliable in the third (sometimes the second) figure after the decimal point. This figure can vary by several units from analysis to analysis.

TABLE 9

The most reliable data on the percentage composition of dry air near the Earth's surface

Gas	% by volume	Gas	% by volume
N_2	78.084 ± 0.004	He	$(5.239 \pm 0.05) \cdot 10^{-4}$
O_2	20.946 ± 0.002	Kr	$(1.14 \pm 0.01) \cdot 10^{-4}$
A	0.934 ± 0.001	Xe	$(8.7 \pm 0.1) \cdot 10^{-6}$
CO_2	0.030 ± 0.003	H_2	$\sim 5 \cdot 10^{-5}$
Ne	$(1.821 \pm 0.004) \cdot 10^{-3}$		

TABLE 10

Average values of the percentage concentration of impurities

Gas	% by volume	Gas	% by volume
H_2O	0.1—2.8	N_2O	$5 \cdot 10^{-5}$
CH_4	$1.5 \cdot 10^{-4}$	O_3	$1 \cdot 10^{-6}$—$1 \cdot 10^{-5}$
CO	$6 \cdot 10^{-6}$—$1 \cdot 10^{-4}$	NO_2	$5 \cdot 10^{-8}$—$2 \cdot 10^{-6}$
SO_2	$1 \cdot 10^{-4}$	Rn	$6 \cdot 10^{-18}$
		NO	Traces

For a final judgment on the constancy of this "expanded" gaseous composition of the Earth's atmosphere, the constancy of the concentrations of the inert gases at various places on the globe had to be investigated. This entailed a new "world-wide" experiment, like that already carried out for the main constituents of the air (oxygen, nitrogen), which proved their concentration to be completely constant; it did not follow from this, however, that the same need be true of the inert gases. Such an investigation had already been carried out for argon, by Moissan /17/ in 1903; his results are shown in Table 11.(The accuracy of the individual analyses was ± 0.002 %).

However, the investigation of the helium content of the atmosphere was of special interest: this is the lightest of all gases except hydrogen, and the

one whose atmospheric concentration is most liable to variation. The point is that helium enters the Earth's atmosphere from the soil, and its rate of entry is by no means uniform: in the neighborhood of oilfields it is extremely high, in other places much lower, and over the sea negligible. There There are also other reasons which make the study of the helium in the atmosphere highly desirable*.

TABLE 11

Origin of sample	A, %	Origin of sample	A, %
Odessa	0.935	Berlin	0.932
St. Petersburg	0.933	Venice	0.936
Athens (USA)	0.935	Paris	0.934
Ionian Sea (37°N, 15°E)	0.936	London	0.933
Vienna	0.938	Atlantic (37°N, 24°W)	0.932
Mean	0.934 ± 0.0006		

Paneth and Glückauf decided in 1935 to carry out a "world-wide" investigation of helium, like those of oxygen, nitrogen and argon previously carried out by Gay-Lussac, Reynolds and Moissan. For this purpose they needed samples of air from widely different parts of the globe.

The determination of helium in air is, as we have already mentioned, very difficult because its concentration is so low; moreover, the planned experiment would only have meaning if a very high accuracy could be guaranteed. Ordinary chemical methods were unsuitable for two reasons: in the first place, they would demand enormous amounts of air, whose transport over long distances would be simply impossible; in the second place, they were not accurate enough. Fortunately, at that time (1933-1935) physicists had already developed equipment for the microanalysis of various gases. In 1912, Langmuir /34/ suggested a "low-pressure" method for the determination of very small amounts of gases evolved from metals and glasses on heating. This method, improved by Ryder /35/, Norton and Marshall /36/, was later widely used for various investigations.

The principle of the apparatus for the microanalysis of gases is as follows. The sample of air under investigation is introduced into a special well-degassed vacuum apparatus. The various gases are separated by making use of various physicochemical properties (boiling point, sorption, chemical affinity, etc.). Measurement of the pressures of the various gases then indicates their concentrations in the original mixture.

Paneth and Glückauf used this method for analyzing their air samples.

Their apparatus is shown in Figure 5. The vacuum apparatus consists of two parts A and B. Part A is used to separate nitrogen and the inert gases from the other constituents of atmospheric air (O_2, CO_2, H_2O, H_2); part B is a fractionation system for separating nitrogen and the various inert gases from each other. The main part of A is a gas burette, into which are introduced two metal spirals (of copper and platinum wire) and small amounts of NaOH and $CaCl_2$ (at G and F). The whole gas burette is placed in a thermostat, to ensure an accurate measurement of the volume of gas in the burette. The air sample is transferred from the bulb in which it is contained to the well evacuated gas burette with the aid of mercury, and

* It should be mentioned that the investigation of the helium content is of prime importance for studying the variation of the composition of the atmosphere with height (see Chapters II and III).

the tap is closed. The H_2O in the sample is now absorbed by the NaOH, and the CO_2 by the $CaCl_2$. The pressure of the remaining air (at a well defined volume) is measured with a mercury manometer. After this, the air is freed from O_2 by heating the copper spiral to 650-700°C: the oxygen combines with the copper, and is completely removed from the air sample. The pressure is then measured again, and the reduction in pressure gives the O_2 content, which was found by this method to lie between 20.93 and 20.96 % for dry air.

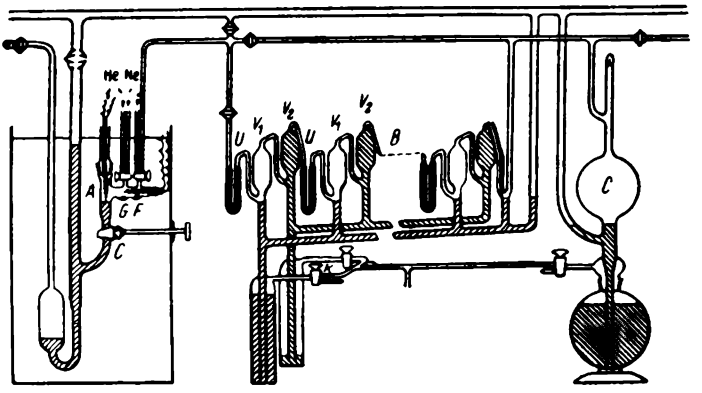


FIGURE 5. Vacuum apparatus for the analysis of samples of air for inert gases (Glückauf and Paneth)

The platinum wire is now heated to remove H_2 and gaseous organic compounds (if present). Measuring the pressure after this process gives the H_2 content of the sample. The amount of hydrogen in pure, dry air is normally very difficult to measure. After the O_2, H_2, CO_2 and H_2O have thus been removed, the rest of the sample, consisting of nitrogen and inert gases, is transferred to the fractionating system (part B, Figure 5) by means of mercury. This fractionating system consists of a series of twelve U-tubes filled with activated carbon, with two bulbs (V_1 and V_2) between each pair of carbon traps; these bulbs serve to drive the gas through the carbon. This is achieved by filling them with mercury, when they act as a Toepler pump. In order to increase the sorption properties of the carbon, the traps are immersed in liquid nitrogen. Helium is the only gas which is not adsorbed (or only slightly adsorbed) by carbon at these low temperatures. This property can thus be used to separate helium from the other inert gases. After the gas has passed through all the traps, the helium is collected in the bulb C. A capillary is sealed into the top of this bulb, and the helium is compressed into this capillary by means of mercury; there it is tested for purity. This is done by applying a high-frequency field to the capillary; the helium then starts to glow, and its purity is checked spectroscopically. The amount of helium obtained is determined by measuring its pressure in a vessel of known volume, with the aid of a modified Pirani gauge (not shown in the figure), as used later by Paneth and Urry /37/. This is a normal small-sized manometer, immersed in liquid air because this makes the zero of the manometer very stable.

Having measured the helium pressure, and knowing the volume of the nitrogen-argon mixture, we can calculate the ratio $He/(A+N_2)$, which can

be used as an index of the constancy of the helium content of the atmosphere (as we have already seen, the concentration of nitrogen [and argon] in the atmosphere is constant).

The careful study by Paneth and Glückauf which we have just briefly described also included an investigation of the possible sources of error of this method of analyzing air. The main question which had to be considered was the extent of the absorption and desorption of helium by glass. It is known that helium can diffuse through glass. The work of Paneth and Peters /38/ showed that this effect is very slight, and would not cause an error of more than 10^{-3}%. The other trouble is that a glass bulb saturated with helium from the air can give off this helium in vacuo, increasing the helium content of the sample above its proper value. Calculations by Paneth, Petersen and Chloupek /39/ showed that in 12 months the contents of the glass bulb (of surface area 300 cm^2) would be increased by 0.3 to 0.5%. However, most of the helium dissolved in the glass can be removed by a preliminary degassing of the bulb. It follows that glass bulbs are quite suitable for storing air samples if the air is at normal temperatures and pressures.

The apparatus described above made it possible to carry out a "world-wide" investigation of helium, which was also suitable for all the inert gases, since there was no reason to believe that their concentrations in the atmosphere should vary more than that of helium. This investigation was carried out as follows /90/.

TABLE 12

Place in northern hemisphere	He · 10^4 %	Place in northern hemisphere	He · 10^4 %
London	5.240	Mariental (Africa)	5.233
Novaya Zemlya	5.250	"	5.253
Krasnoyarsk	5.245	Antarctica	5.227
California	5.238	"	5.231
Orono (USA)	5.239	Rio de Janeiro	5.250
Panama Canal	5.240	Pandang (Sumatra)	5.232
Caribbean Sea	5.243	Wellington (New Zealand)	5.250
Atlantic Ocean	5.233		
Mean	5.240	Mean	5.239

Special glass bulbs (capacity 200–300 cm^3) with rubber bungs were sent to various parts of the Earth. Instructions were sent with the bulbs to the effect that the bulbs should be filled (to the top) with pure water, and then emptied again. Finally the bulbs should be closed with the rubber bungs, and sealed with a type of sealing wax, this being the simplest reliable method of obtaining a good sample. Since the samples were only analyzed for helium and nitrogen, the water left in the bulbs did not introduce any error, since neither helium nor nitrogen react with it. The results of the analyses are shown in Table 12. It was shown that the mean helium concentration in both hemispheres was $5.239 \pm 0.002 \cdot 10^{-4}$%.

After such a complete and accurate investigation, there could no longer be any doubt that air really is a gaseous mixture of constant composition.

Conclusion

In this chapter we have considered the first stage of the investigation of atmospheric air, which took many times longer than all later stages. This is perfectly normal: the history of all branches of science (not only relatively small problems like that of the composition of the air) shows similar phenomena. Problems which used to take centuries to solve are now cleared up in decades, or even a few years. The investigation of the lower atmosphere is an excellent example of this: it took thousands of year to "discover" air, hundreds of years to "understand" it, and decades to investigate it in detail.

It is hoped that the material contained in this chapter will give some idea of the great significance of the early problems concerned with the investigation of air, which led to the modern chemistry of gases and freed science from the myth of phlogiston. It is difficult to overestimate the importance of this preliminary work and the gaining of reliable data on the composition of the lower atmosphere for geophysics in general and the problem of the gravitational separation of gases in particular. The proof of the constant composition of air at the Earth's surface provided a firm basis for solving the problem of the variation of this composition with height.

Chapter II

INVESTIGATIONS OF THE COMPOSITION OF THE MIDDLE ATMOSPHERE (up to a height of 30 km)

Introduction

The investigation of the composition of the atmosphere at different heights began even before the determination of the air composition at the Earth's surface was completed. The stimulus to such a series of investigations was given by the propounding of Dalton's law of partial pressures (1802). Since it was known that air is a mixture of different gases, it followed from Dalton's law that one could expect a separation of gases in the gravitational field of the Earth, the heavier gases being concentrated near the surface of the Earth and the lighter ones at higher levels.

A number of scientists, beginning with Dalton himself, investigated the composition of the atmosphere at various altitudes in the hope of obtaining experimental confirmation of the law of partial pressures. Techniques for the chemical investigation of samples of air had already been worked out by this time (see Chapter I). However, matters were complicated since it was impossible to collect large samples of air at high altitudes. The scientists also had no means of reaching altitudes higher than accessible mountain peaks.

The first attempts to demonstrate the gravitational separation of gases in the atmosphere began in 1801-1803, with the investigation of "mountain air". The investigators climbed as far as possible up a mountain and collected a sample of air. The sampling was normally carried out rather primitively, the samples being collected in an ordinary bottle which was not always clean. The bottles were corked, and sealed with sealing wax. Analysis was not always immediate, since it was considered that air could be stored in a sealed bottle indefinitely without "spoiling". The samples were analyzed for oxygen, since this was the lightest component of the air and could be determined most accurately; the remainder of the sample was taken to be nitrogen.

As might be expected, the results obtained in this way were highly contradictory and were interpreted in a very arbitrary manner. Evidence for the separation of gases by diffusion was found by those who wanted it, and not detected by those who did not. However, no one found the quantitative separation predicted by the law of partial pressures.

Dalton's analyses of samples of air which he himself collected at heights of from 1-3 km showed a certain decrease in the oxygen content compared to that at sea level. Dalton regarded this as a qualitative confirmation of his law, though quantitatively the decrease in the oxygen content did not

agree with that deduced from his law. Dalton quite rightly explained the deviations from this law as being due to the action of winds. After Dalton, others carried out similar large-scale investigations. For example, Boussingault /40/ in America found that at heights of 548, 1323, and 2650 m above sea level the percentage of oxygen in the air was 20.77, 20.70, and 20.65 respectively. These results were at that time taken as confirmation of the gravitational separation of gases at these heights. However, analyses of samples of "mountain air" carried out by other investigators (Saussure, Humboldt, etc.) at this time showed no difference between the composition of this air and ordinary air. Such differences in experimental results produced a certain amount of pessimism among scientists at that time, and even the law of partial pressures itself was doubted.

The main reason for the differences between the results of different investigations lay in the insufficiency of the experimental methods used. As we have mentioned, the samples of air were analyzed for oxygen. However, that property of oxygen which facilitated its analysis (its great chemical activity) also made it easy for oxygen to be lost from the sample while still in the bottle, as a result of chemical reactions (oxidation). Also, the bottles containing the samples were closed with a cork (made from the bark of a tree) and sealed with sealing wax. It is only to be expected that there would be a loss of oxygen from such unsuitable containers. The failure to take these factors into consideration led to the above-mentioned differences in the analyses of "mountain air". Observed decreases in the oxygen content of samples were interpreted by prejudiced investigators as confirmation of the law of partial pressures. However, many scientists did not share this opinion. The problem of the composition of "mountain air" was therefore sharply debated for a long time. In order to solve this problem, it was necessary to extend the investigations to higher altitudes and to increase the accuracy of the analyses considerably.

1. Balloon ascents

A great scientific event at the end of the 18th Century was the invention of the balloon. The first balloon ascent was made in Paris on 27 August 1783, in a hydrogen-filled balloon invented by the French physicist I. A. Charles. Despite the fact that the first flights were made solely for pleasure, prominent scientists recognized the balloon as a new and powerful means of investigating the atmosphere. Thus, Priestley wrote in a letter to Banks that the balloon, which "at present is an idle diversion, may in time answer important philosophical problems by allowing us to investigate the upper regions of the atmosphere" /41/. It was in fact not long before the balloon was used for various investigations of the atmosphere and the composition of the air at high altitudes.

On July 1804 the Russian academician Zakharov /42/ made the first balloon ascent in which special bulbs were taken up for sampling the air. Three months later, Gay-Lussac made a balloon ascent /43/. He reached a height of 7000 m and obtained a sample of air, which on analysis contained the same oxygen content as air at the surface of the Earth. This may be considered to be the beginning of the investigation of the atmosphere at "great" altitudes.

In 1853, Welsh made a balloon ascent and collected samples of air at a height of 5680 m. These samples, analyzed by Müller /44/, gave 20.89 % O_2 at 4080 m, 20.82 % at 5550 m and 20.92 % at ground level, thus indicating a certain decrease in the O_2 content with height.

In 1875, Mendeleev turned his attention to the study of the composition of the atmosphere /45, 46/. Comparing the experimental results with the theoretical variation of the partial pressure of oxygen with height (calculated for a completely calm and dry atmosphere), Mendeleev came to the conclusion that the results so far obtained were inconclusive. His calculations showed that even in a completely calm atmosphere the variation of the oxygen content up to a height of about 5 km was virtually negligible. Since the winds which were known to occur at these heights caused mixing, the variation should become vanishingly small. According to Mendeleev, results could only be obtained at considerably higher altitudes.

High altitude ascents in balloons were rare, not only because of the great expense but also because of the considerable danger involved. Many investigators lost their lives in attempts to reach "forbidden" heights. Therefore, attempts were made to send up small balloons carrying automatic equipment; this was the first use of "sounding balloons", which were later to play a decisive part in the investigation of the stratosphere.

In 1897, probably for the first time in history, Cailletet sent up an automatic sampler with one of these small balloons, and obtained a sample of air from 15,500 m. This was considered an enormous height at that time /47/. The vessel had a volume of about six liters and was made of copper for strength: a glass vessel of the same volume would be sure to break during the descent. The analysis of the air sample obtained in this way gave 20.79 % O_2, 78.27 % N_2 and 0.94 % A. Here too, as with Welsh, a very small decrease in oxygen content was found. However, it was clear that Welsh and Cailletet could not both be right since they had found practically the same decrease in the oxygen content at 5500 and at 15,500 m. Such results from two completely different experiments were mutually exclusive: if Welsh were right, then Cailletet's sample should have contained considerably less oxygen; if Cailletet were right, then the decrease in the oxygen content found by Welsh must have been due to experimental error. The disagreement was magnified because Cailletet admitted that an error might be caused by the walls of the copper vessel absorbing oxygen, even at normal temperatures. Thus, the result of the analysis of the sample taken from 15,500 m could probably be taken as a direct proof of the constant composition of the atmosphere up to this height. This possibility did not agree at all well with the prevailing view of the structure of the atmosphere, and was greeted with extreme scepticism. Moreover, the first automatic samplers were not sufficiently reliable to inspire great confidence. Consequently, a correct conclusion about the mixing of the atmosphere, at least up to the height attained by Cailletet, was not reached.

After Cailletet, Teisserenc de Bort in 1908 was the next to use automatic sampling devices carried by sounding balloons /48/. He, like Cailletet, found no change in composition up to 10 or 12 km above the Earth. The vessels used by Teisserenc de Bort were made of glass, and had volumes of one or two liters. Owing to the small sample size a very accurate analysis of the composition of the air could not be carried out, but it was still clear that there was no appreciable separation of gases up to these altitudes.

2. Discovery of the stratosphere and the problem of the gravitational separation of gases

The advances in molecular physics at the end of the 19th Century left no doubt as to the correctness of Dalton's law of partial pressures. The absence of gravitational separation in the atmosphere up to such high altitudes therefore caused scientists some perplexity.

The discovery of the stratosphere in 1893 considerably changed our views on the structure of the atmosphere. This discovery, confirmed by Teisserenc de Bort in 1901-1903, also threw a completely new light on the problem of mixing. As is known, the stratosphere is the name given to a region of the atmosphere above 7-9 km where, surprisingly, the temperature does not change with height, while at lower levels (the troposphere) the temperature falls by about 5 or 6°C for every kilometer. The existence of the stratosphere, which was confirmed beyond any doubt by investigators after Teisserenc de Bort, led to the idea that the troposphere is thermally unstable, and that its layers continually tend to mix; the stratosphere, on the other hand, where this vertical movement should be absent, might be expected to be stable.

It would seem to follow from this that the height at which gravitational separation may be expected to begin coincides with the lower boundary of the stratosphere. This point of view fitted in well with other ideas about the structure of the atmosphere, but in order to confirm this experimentally it was necessary to carry out an accurate investigation of the composition of the air above the lower limits of the stratosphere. This was technically impossible to do at that time. The matter was further complicated by the discovery that the height of the troposphere depended both on the latitude and the time of year. Therefore, even with ascents to 9-11 km it would sometimes be difficult to decide whether the observation was made in the troposphere or the stratosphere.

As a result of these views, the above-mentioned work of Cailletet, in which the samples of air were clearly taken from the "unmixed" stratosphere, was greeted with considerable doubt by his contemporaries. On the other hand, the work of Teisserenc de Bort, where the samples were taken from the upper troposphere, was regarded as a good confirmation of the ideas about the mixing of the troposphere.

The search for the limit of the gravitational separation of gases now had to be shifted to even higher layers of the atmosphere. The difficulties involved in extending the investigations to higher altitudes were so great, however, that it was some considerable time before this could be done. A great mistake which had been made in all investigations so far mentioned was to analyze the air for oxygen and nitrogen. In fact these substances are very unsuitable for this purpose since their molecular weights differ so little. Moreover, it became clearer and clearer that great care had to be taken in the determination of oxygen, and that the oxygen content of the sample did not always correspond to that in the atmosphere. Besides this, as we have already mentioned, the amount of air collected on the flights was very limited, and this considerably reduced the accuracy of the analyses. The relatively low accuracy of the determinations of O_2 and N_2 combined with the very slight variations in the O_2/N_2 ratio cast doubt on all experiments carried out in this direction. Some way out of this impasse had to be found.

At the beginning of the 20th Century, scientists had learnt how to determine (although rather crudely) the total content of light gases in air and they began to analyze air samples for these light gases /49, 50/ in the hope of obtaining clearer indications of gravitational separation. CO_2, which could be determined quite accurately (see Chapter I), was used as a heavy gas in these investigations. The work of Tetens and Wigand is typical of the investigations carried out at this time. In 1910, Tetens /51, 52/ ascended to 8000 m in a hydrogen-filled balloon, and took samples of air. These were analyzed for the light gases (sum of H_2+Ne+He) and gave 26.2 mm^3/liter at a height of 80 m, and 37.7 mm^3/liter at 8000 m*. This is an enormous difference — an increase of 44 % in 8 km — and not surprisingly, was met with suspicion, even by those who were convinced of the existence of gravitational separation near the Earth's surface. Such a rapid increase in the content of light gases was in excess of that predicted by Dalton's law. It was suggested that the samples contained some hydrogen from the balloon.

In 1913, Wigand /53/ decided to repeat Tetens' experiments, while taking all possible precautions to avoid his errors. The experiment was performed as follows. A two-liter glass bulb with a three-way vacuum tap was evacuated, tested for leaks, placed in a special safety box, and then suspended outside the gondola of the balloon. In order to obtain as pure a sample as possible, the air was collected through a long (30 m) aluminum tube connected to one limb of the three-way tap of the glass bulb; the second limb of the tap was fitted with a rubber bulb. The aluminum tube (which was made of several lengths screwed together) hung down out of the gondola to prevent gas in the balloon from entering the sample. Before a sample was taken, the tube was connected via the tap to the rubber bulb and the air

TABLE 13

Height, m	Content CO_2, mm^3/liter	Content H_2+Ne+He, mm^3/liter	H_α spectral line of hydrogen
5750	294.1	22.8	Distinct
6250	283.6	27.1	–
6350	278.3	24.5	Distinct
9040	277.05	33.7	Strong

pumped to and fro to ensure that the sample did not contain air from a different level. The tap was adjusted to connect the tube and the flask and the air filled the flask. The sampling was carried out while the balloon was at a constant height, or descending slowly. Since the samples were also to be analyzed for CO_2, precautions were taken to prevent CO_2 exhaled by the aeronauts from entering the sample. They breathed through special masks which absorbed CO_2.

Wigand reached a height of 9040 m in his ascents, and took a number of samples, which were analyzed by Erdman /49, 50/. The results are given in Table 13.

If we consider that the concentration of "residual gases" (H_2+Ne+He) at the Earth's surface is 26.3 mm^3/liter, and that of CO_2 is 300 mm^3/liter, we may conclude from the above results that the CO_2 content decreases with

* It should be noted that the volume of the air sample taken at 8000 m was no more than 360 cm^3.

height, while that of the light gases increases. Wigand concluded from these results that gravitational equilibrium was not yet reached, even at the heights he had attained, but that there was still a definite separation.

Thus, the experiments of Wigand "confirmed" the increase in the concentration of light gases with height, "discovered" by Tetens. Evidence confirming this increase had also been found by Konshegg and Gashek /54/, who observed a fairly strong H_α line during the spectral analysis of air samples taken at 7800 m (Erdman had also made a similar observation). They mistakenly attributed this line to hydrogen in the atmosphere. Later, more careful analysis showed that the "residual gases" consisted mainly of hydrogen. As we now know very well, this hydrogen came from the balloon. It is quite natural that as the balloon ascends, it should introduce an increasing amount of impurities into the atmosphere. This increase was taken as the real increase in the concentration of light gases with height.

Wigand's careful experiment with the 30 meter tube clearly showed that turbulence plays an important role in the atmosphere. The ascending balloon was surrounded by an enormous cloud of stray gases. Even though they were lighter than air, the turbulent mixing was enough to pollute the air quite a way under the balloon with these gases. In Wigand's experiment, considerable amounts of hydrogen found their way to 30 m under the gondola, giving a highly falsified picture of the concentration of this gas in the atmosphere.

The same argument holds for the spectral analyses of Erdman, Konshegg and Gashek. Moreover, the results of these experiments might have been influenced by moisture in the sample or in the analytical apparatus. Water vapor dissociates into oxygen and hydrogen in a gas discharge, and the hydrogen thus produced reinforces the H_α line in the spectrum.

Despite the unsatisfactory nature of the work described above, the results obtained were regarded by most geophysicists at that time as definite evidence that gravitational separation began to play a predominant role at a height of 7–9 km above sea level /33/. Now that there was no longer any doubt about the truth of the law of partial pressures, experimental geophysicists regrettably went to the other extreme and even accepted without due examination doubtful results which seemed to confirm the operation of this law in the atmosphere.

3. Early investigations of the composition of the atmosphere at high altitudes by indirect methods

We shall now give a brief account of the results of some investigations carried out by indirect methods. This is important because the indirect methods, used in the 1920-30's for investigating the upper levels of the atmosphere, led to conclusions which differed radically from those obtained by direct methods, in particular to the conclusion that the atmosphere is mixed up to very high altitudes. There was, therefore, considerable disagreement among investigators at the beginning of the 20th Century as to the nature and composition of the upper atmosphere; in fact, this peculiar "dualism" was not resolved until quite recently.

Two atmospheric phenomena occurring at high altitudes allow us to draw certain qualitative conclusions about the composition of the upper

atmosphere: the polar aurora and the airglow*. The spectra of these two phenomena indicate the gases present at heights of about 100 km which cause this luminosity. By this time the presence of nitrogen molecules had been demonstrated in the region of the polar aurora, at heights of 100 km. Moreover, the same spectra contained a bright green line (5577 Å) which could not be assigned to any known gaseous molecule for a long time. The fact that nitrogen molecules were present at such great heights was a hard pill to swallow for those investigators who held that separation by diffusion, starting from 7–9 km above the Earth, should "limit" nearly all the nitrogen to heights not exceeding 50–70 km. However, since there was no way of obtaining any quantitative data on this point, the problem of the mixing of the atmosphere still evaded solution. The puzzling green line in the spectra led A. Wegener /41/ to suggest that a hitherto unknown very light gas, which he called "geocoronium", was present in the upper layers of the atmosphere and was responsible for this line. This hypothesis was however short-lived.

In 1925, Vegard /55/ suggested that the green line might be caused by the exposure of "frozen" nitrogen to cosmic electrons. However, this suggestion also proved false. The experiments of McLennan /56/ clearly showed that the green line was due to atomic oxygen. This unexpected solution to the problem of the green line disposed of the geocoronium hypothesis, and indicated that the upper layers of the atmosphere contain not only molecular nitrogen but also atomic oxygen**.

Another unexpected finding was that neither the spectrum of the polar aurora nor the airglow showed any signs of emission by the light gases helium and hydrogen. Although this did not prove that the light gases were not present in the atmosphere at these altitudes***, it did make it highly unlikely that the gravitational separation of gases began at a low level. The theoretical work of Maris /57, 58/, carried out in 1928, indicated that the limit of gravitational separation occurred at about 100 km.

The work just described was thus in contradiction with the view, firmly held by the majority of scientists, that the limit of gravitational separation was somewhere near the bottom of the stratosphere. In order to clarify the position, it was necessary to carry out direct investigations at altitudes considerably higher than those reached so far.

4. Direct investigations in the stratosphere

The first systematic investigation of the air in the stratosphere was carried out by Lepape and Colange in 1927 /59-61/. Learning from the attempts of the previous investigators (Cailletet and Teisserenc de Bort), they did their best to reduce the weight of their equipment to the minimum, so that the balloon could ascend as high as possible. They used thin-walled

* For further details see the book: Khvostikov, I. A. Svechenie nochnogo neba (Luminosity of the Night Sky), Moskva. 1948.

** It is interesting to mention that about the same time, astronomers discovered two bright green lines of unknown origin (λ = 5007 and 4950 Å) in the spectra of the planetary nebulas. These lines were ascribed to a new element "nebulium". However, a careful investigation by Bowden in 1927 showed that these two lines are due to forbidden transitions of doubly ionized oxygen atoms. Thus oxygen, first in the guise of "geocoronium" and then as "nebulium", twice misled scientists.

*** Light gases, while present, may not become excited for one reason or another, thus emitting no radiation.

glass bulbs (volume 1 liter) provided with two side arms, one for the preliminary evacuation of the vessel, and the other for taking the air sample. The latter consisted of a tube 5–7 cm long and 6 mm in diameter, with a ground glass joint so that it could be connected to the inlet of the analytical apparatus. This tube ended in a capillary 10 cm long and 0.5 mm in diameter. The bulb was first evacuated to 0.01 mm Hg; at the moment of sampling, the end of the capillary was broken and air entered the bulb. The bulb was opened and closed using smouldering tinder, which was lit before the sounding balloon's ascent. At a given moment (calculated), the tinder burnt through a thread which had been holding back a little spring-loaded hammer and now broke the capillary. The tinder then ignited a combustion mixture. A special cement surrounding the capillary was thus melted and sealed the bulb. Special precautions were taken to ensure that the combustion products did not enter the bulb: during the sampling time (1 minute), 0.1 g of tinder were consumed, and in this time the balloon rose 200 m; the air-flow conditions were thus such that the fumes would have no chance of mixing with the sample. Moreover, before sealing, the temperature of the bulb was raised to 20°C, so that at the moment of sealing some gas was flowing out of the bulb, thus preventing impurities from entering.

A Teisserenc de Bort recorder was also sent up with the balloon; this recorded the pressure and temperature of the surrounding air at the moment of sampling. Two bulbs were normally used in each experiment; they were placed in an ordinary wicker basket to cushion their fall. The weight of the entire equipment sent up did not exceed 600 g, thus allowing ascents to be made up to about 12–16 km.

To remove the air from the bulb, the ground joint with the sealed capillary on the end was connected to a tube with a matching joint. This tube, which contained a special metal weight, was closed at the other end with a tap. After the tube had been evacuated, the tap was closed and the whole system (bulb + tube) was shaken vigorously. The weight broke the capillary and the air escaped into the tube. The tube was connected to the analytical apparatus and the tap opened. The air sample was then allowed to flow into the apparatus for analysis.

The samples were analyzed for CO_2, O_2, N_2, He + Ne, and A + Kr + Xe. Special care was taken with the analysis for O_2 and Ne + He. For the analysis of the small quantities of gas involved, Lepape and Colange used a special glass apparatus designed by Muro and Lepape. This apparatus was a closed system containing a mercury manometer and a small bulb containing electrolytically pure copper, the latter being surrounded by an electric heating coil. The bulb containing the copper was connected to the manometer via a trap cooled in liquid oxygen. In order to keep volumes accurately constant, the system was immersed in a water thermostat.

The analysis for oxygen used 10 cm^3 of the sample at normal temperature and pressure (N. T. P.). The gas was first passed through a coil cooled in liquid oxygen, thus removing ("freezing out") water vapor, carbon dioxide and all organic impurities. The pressure was then measured carefully. The gas was circulated for half an hour over the copper, which was heated to dull redness, thus removing all the oxygen. The pressure of the remaining nitrogen was carefully measured. Knowing the volume of the gas accurately, the oxygen content could be calculated from the difference of these two pressures.

From 50–150 cm^3 of the sample (at N. T. P.) were used for the determination of the inert gases. The oxygen and nitrogen were removed by absorption on metallic sodium, and the separation of the inert gases was carried out on coke cooled in liquid oxygen.

Table 14 gives the results of the analyses of 12 samples taken at different times and at different heights.

TABLE 14

Date	Height, km	Concentration, %			
		O_2	N_2	inert gases	$(He+Ne)\cdot 10^4$
1 August 1927	11.6	20.99 ±0.06	78.08	0.932	3.2
12 December 1927	14.2	20.965 ±0.05	78.13	0.911	3.5
16 December 1927	16.8	21.32 ±0.04	77.74	0.941	
29 December 1927	13.0	20.80 ±0.04	78.26	0.945	-
21 June 1928	16.2	20.99 ±0.005	78.06	0.952	3.3
22 May 1928	9.6	20.93	78.13	0.944	2.8
22 May 1928	9.0	20.84 ±0.01	78.24	0.923	
17 August 1928	12.8	20.85 ±0.005	78.22	0.934	-
17 August 1928	10.0	20.87 ±0.005	78.19	0.937	4.6
26 November 1929	14.9	20.80 ±0.02	78.26	0.942	-
26 November 1929	11.2	20.81 ±0.02	78.26	0.927	2.7
18 August 1934	15.0	20.90 ±0.05	78.16	0.940	3.0
Mean	-	20.92	78.15	0.935	3.3

Lepape and Colange also analyzed 9 of these 12 samples for water and carbon dioxide /62/. The water content was found to vary between 0.1 and 0.4 mm Hg; however, as Lepape and Colange rightly remarked, the real moisture content of the samples must have been higher than this, since the walls of the analytical apparatus and of the sampling bulb avidly absorbed water vapor. The bulb was not heated during the analysis, so the absorbed water remained on its walls. The carbon dioxide was removed from the air by freezing; the amount of CO_2 found in the various samples is shown in Table 15.

TABLE 15

Date	Height, km	CO_2 content, %	Date	Height, km	CO_2 content, %
22 May 1928	9.0	0.05	17 August 1928	12.8	0.05
22 May 1928	9.6	0.04	26 November 1929	14.9	0.03
17 August 1928	10.0	0.06	18 August 1934	15.0	0.08
26 November 1929	11.2	0.06	21 April 1928	16.2	0.13

On the basis of these results, Lepape and Colange came to the following conclusions:

1. The hypothesis of the gravitational separation of gases with height should be rejected (at least for O_2 and N_2), since no separation was found.

2. The ratio Ne+He to the sum of inert gases was found to be somewhat higher at the altitudes investigated than at ground level.

3. Unlike Teisserenc de Bort, they found helium in their samples (by spectral analysis).

4. The CO_2 content increased with height.

5. The atmosphere was supersaturated [sic.] with water vapor.

These conclusions are quite interesting, although, except for the first one, they do not agree very well with our present conceptions of the atmospheric composition at altitudes of 10–15 km.

At the heights investigated (9–16 km), Lepape and Colange "succeeded" in finding an increase in the content of light gases with height, thus strongly confirming the opinion of earlier investigators of this problem (Tetens, Wigand). The concentrations of water vapor and CO_2 found can easily be explained since both these substances are very difficult to remove from the gas-analysis apparatus. Therefore, errors are bound to arise in the determination of very small amounts of these gases.

5. Balloon ascents into the stratosphere

At this time, the investigations of the upper atmosphere were becoming more intensive each year. It became necessary to convey equipment to

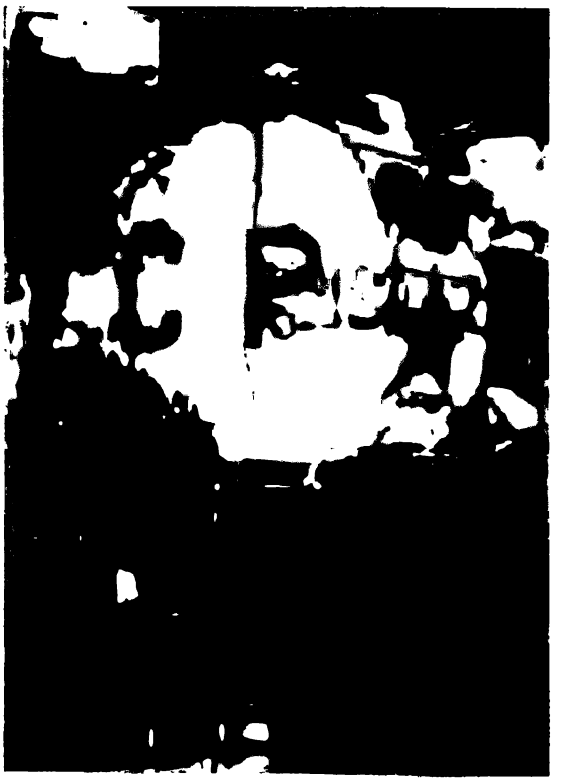


FIGURE 6. The gondola of the stratosphere balloon "SSSR" [CCCP in Russian]

high altitudes not only for the chemical analysis of air but also to investigate cosmic radiation, the ultraviolet radiation from the Sun, the conductivity of the air, etc. The necessary equipment was very heavy and therefore could not be carried by sounding balloons. This naturally gave rise to the idea of carrying the equipment and the observers to high altitudes in the sealed gondola of a large stratosphere balloon. Such a gondola would be a flying laboratory for complex investigations of the physical parameters of the stratosphere.

As is well known, Professor Picard was the first to make an ascent in a hermetically sealed gondola (to a height of 16 km), in 1931. This flight was not a great success, and Picard narrowly escaped death. In his second ascent (1932), Picard reached a height of 16,500 m and obtained interesting data on the intensity of cosmic rays. However, the ascent of the Soviet stratosphere balloon "SSSR" /63, 64/ on 30 September 1933 shed light on many properties of the upper atmosphere. This balloon (see Figure 6) carried scientific equipment for a wide program of investigations, and reached the record height of 19 km.

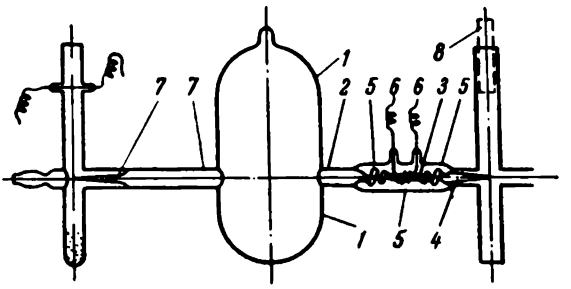


FIGURE 7. Shal'nikov and Gol'tsman's glass sampling vessel

1–bulb; 2–side arm for entry of sample; 3–capillary; 4–sealed-off end of capillary; 5–jacket containing air; 6–platinum heating coil; 7–side arm for connecting the bulb to the analytical apparatus; 8–weight.

For the very first time three Soviet investigators (G. A. Prokof'ev, E. K. Birnbaum and K. D. Godunov) thus succeeded in penetrating deep into the stratosphere and carried out a series of valuable experiments there. Their program included the taking of samples of air; for this purpose they used a sampler designed by A. I. Shal'nikov and M. I. Gol'tsman (Figure 7). The sampler was placed in a special metal case outside the gondola, in such a way that gases given off by the envelope of the balloon could not contaminate the sample taken. The electricity supply for the devices for opening and closing the sampler was inside the gondola. The sampler consisted of a glass bulb 1 of capacity 1 liter, with two side arms 2 and 7; side arm 2 was for the entry of the sample of air, and 7 for connecting the bulb to the analytical apparatus. Before the ascent, the bulb was carefully evacuated to a pressure of 10^{-5} mm Hg, and sealed. When the balloon had reached its maximum height, the closing of a special relay released the weight 8, which in its fall broke the end 4 of the capillary so that the surrounding air entered the "empty" bulb 1. After some time, the platinum heating coil 6 was switched on, thus melting the capillary 3. The air contained in the jacket 5 pressed the molten glass of the capillary together,

sealing off the bulb. In order to prevent hydrogen emitted by the balloon from contaminating the sample, sampling was carried out while the balloon was descending slowly. The analysis of the samples obtained, carried out in parallel by A. V. Moskvin and A. A. Cherepennikov /63, 67/, gave identical results:

1. The pressure in the balloon was 47.5 ± 0.2 mm Hg (referred to $T = -55°C$).
2. No hydrogen was found.
3. The oxygen content at a height of 18,500 m was 20.95 %.
4. The content of nitrogen + inert gases was normal (79.05 %).

The results of this experiment, whose validity there is no reason to doubt, indicate that the sampled air was completely identical with the air at the Earth's surface. This result was so unexpected that it was necessary to make quite sure that the bulb really did contain stratospheric air. For this purpose, the moisture content of the bulb was checked by the dew-point method (mirror cooled by liquid oxygen). The air in the bulb was found to be completely dry, which confirmed its stratospheric origin.

The flight of the stratosphere balloon "SSSR" thus distinguished itself from all previous investigations (in which an increase in the content of light gases with height was "observed") in that here the composition of the air at a height of about 20 km was found not to differ from that at ground level. This finding of Soviet investigators has stood the test of time, and is now firmly established in our wealth of scientific knowledge on the atmosphere.

This finding cast some doubt on the firmly held view that the stratosphere was free from vertical currents which could mix the air at different heights. The level of gravitational separation was thus raised again, and it was now quite clear that it lay right out of the troposphere. In order to find the height where gravitational separation began, it was once again necessary to ascend still higher. This feat was achieved by another Soviet stratosphere balloon, the "Osoaviakhim"*, on 30 January 1934.

The "Osoaviakhim", like the "SSSR", was equipped with special bulbs for sampling the air. The bulbs (Figure 8) were placed inside the gondola and were connected to the outside air by a special duct. The bulbs were opened and closed from the cabin by means of an electric current. The ascent of this balloon, which reached a record height of 22,000 m, ended in disaster and the entire crew was killed. The bulbs containing the samples of air were lost in the disaster, so this outstanding ascent gave no new information about the composition of the atmosphere at high altitudes.

In order to complete our description of the investigations of the composition of stratospheric air carried out by stratosphere balloon, we shall depart slightly from the chronological order and describe the ascent of the American balloon "Explorer II", which in 1935 reached a record height of 22,060 m /143/. This ascent was undertaken by the Americans not so much in the interests of science as with the aim of establishing a new sporting record. They reached a height of 22 km at an enormous risk, and reached terra firma again in safety, although several times during the ascent they were on the brink of disaster. Samples of air were taken at a height of 21.5 km at the beginning of the descent. The samples were taken in three glass bulbs of volume 22 liters each (Figure 9), enclosed in special metal

* [Obshchestvo sodeistviya oborone i aviatsionno-khimicheskomu stroitel'stvu SSSR (1927-1948) (The Society for the Promotion of Defense and the Aero-Chemical Development).]

FIGURE 8. The air-sampling devices used in the stratosphere balloon "Osoaviakhim"

center–the sealing device for the bulbs; right–a sealed inlet tube

casings. The space between the glass and the metal casing was filled with an elastic substance to absorb shock. The bulbs were placed inside the gondola, and were connected with the outside air by means of special taps. Unfortunately, the inlet of one of the taps was blocked with grease at the moment of sampling, so that the air could not enter that vessel. The two other bulbs were filled without mishap. As in other flights, the samples were taken at the beginning of the descent. However, as the analysis of the samples showed, this was apparently not enough to prevent contamination by gas from the balloon: the samples were found to contain an enormous amount of helium (the gas used to fill the balloon), 50 times more than could be expected. This result once more (cf. Vegard's* experiments) showed that a balloon floating in the atmosphere is surrounded by a great cloud of "poisoned" air, which considerably reduces the value of the experiment. As regards the oxygen and carbon dioxide in the samples, analysis /89/ gave the following values: CO_2 – 0.029 ± 0.002 %, and O_2 – 20.895 ± 0.003 %.

FIGURE 9. Bulbs used for sampling air in the stratosphere balloon "Explorer II"

The cap of the left-hand container has been removed to display the glass tube with tap leading to the inner glass bulb

As may be seen from these results, the carbon dioxide content at an altitude of 21.5 km is the same as at ground level (0.03 %), while the oxygen content is slightly lower (20.945 % at the Earth's surface). This decrease is is however so slight that it can hardly be taken as definite evidence of a decrease in the oxygen content at these altitudes. Bearing in mind the reliable results obtained with the "SSSR", the investigators concluded that the composition of air at an altitude of 21.5 km is identical with that at the Earth's surface.

After this series of successful and unsuccessful ascents by balloon into the stratosphere from 1931–1935, it became perfectly clear that these flights, which were attended by such great threats to the lives of the investigators, were highly undesirable. This, combined with the complexity of the experiments and the expense and difficulty of raising the ceiling of the

* [Apparently Wigand is intended.]

investigations, put a stop to work of this kind. The ascent of "Explorer II" was the last of its kind, leading investigators to turn their energies to improving methods involving the use of sounding balloons. As we shall see below, much simpler and safer methods could give more complete information about the composition of the air at high altitudes.

6. Sounding-balloon investigations with automatic equipment

Returning to the chronological order in our description of the investigations of the composition of the air, we come to the investigation of Paneth and Glückauf carried out in 1935 /65/. Agreeing with previous workers that chemical analysis of the air was the best means of discovering gravitational separation of gases in the atmosphere, Paneth and Glückauf reasonably pointed out that analysis for oxygen and nitrogen was not sensitive enough for this purpose, because of the slight difference in molecular weight of these two gases. Much better results should be obtainable by analyzing for hydrogen and nitrogen, or hydrogen and argon. However, a reliable determination of the minute amounts of hydrogen present in the samples collected from high altitudes was hardly possible, for the following reasons. As we have mentioned above, it was very difficult to remove traces of "stray" hydrogen from the vacuum apparatus: the water in the glass walls and the grease of the taps constantly gave off minute amounts of hydrogen. Moreover, the apparatus also contained traces of water even after thorough heating. The evolution of hydrogen from the walls naturally had a particularly adverse effect on the accuracy when small samples had to be analyzed. In this case, the impurities may exceed the gas being analyzed tenfold, and naturally this gives a highly distorted picture of the amount of hydrogen present in the atmosphere. Moreover, the analysis of samples of air from high altitudes for hydrogen may be in error due to the presence of moisture in the atmosphere itself. When a degassed bulb is filled with moist air the moisture is very strongly absorbed by the glass walls; but even a slight increase in temperature is sufficient to cause some of the absorbed water to be given off again. Taking all this into account, Paneth and Glückauf decided to base their work on the analysis of the helium in the air, this being the next lightest gas after hydrogen. Analysis of the samples for helium is particularly attractive because, being chemically inert, helium does not react with anything. Therefore, the helium content of the sample, if determined by a reliable method, will be equal to the real helium content of the atmosphere. However, in order to tackle the problem in this way they had to learn how to determine with accuracy the very small amounts of helium present in the air (the concentration of helium in the air near the Earth is about $5 \cdot 10^{-4}$%: see Chapter I).

As we have seen, the analysis for helium of samples of air taken from near the Earth's surface was done with fair accuracy. However, the situation became more complicated when the investigation had to be carried out on very small portions, since in order to reach high altitudes (20 km and more), the weight of the sampling bulb (and thus its volume) had to be very strictly limited. Moreover, the density of air at a height of 20 km is only about one tenth of that at ground level, so that the volume of an air sample collected from a height of 20 km did not exceed some tens of cubic centimeters (at N. T. P.).

Making use of the work of Paneth and Peters /66/ and Paneth and Urry /37/, Paneth and Glückauf were able to determine the helium content of air samples, not more than a few cm^3 in volume (at N. T. P.), to within an accuracy of a few hundredths of a percent of the total volume.

They collected their samples in a glass bulb which, like that of Lepape and Colange, had two side arms, one for the inlet of the sample and the other for transferring the air to the analytical apparatus. At the highest point of the ascent (after the balloon had burst), the end of the glass side arm was broken and the surrounding air entered the evacuated bulb. This took about 10–15 seconds, during which time the bulb was falling slowly on a special parachute. The broken-off end of the capillary was then sealed again. A special barothermograph recorded the pressure at the time of sampling; this recording allowed the height of sampling to be estimated. If the mechanism worked properly, the pressure inside the bulb should be equal to that outside it*. The results of the successful measurements carried out by Paneth and Glückauf are given in Table 16. In this table

TABLE 16

Height *H* according to barothermograph, km	Height *H* according to pressure in bulb, km	$He \cdot 10^4$, %	$\frac{He_H - He_{H=0}}{He_{H=0}}$ *, %
–	0	5.27 ± 0.05	–
16.8	14.0	5.35 ± 0.07	1.7 ± 1.4
18.5	18.4	5.31 ± 0.05	0.7 ± 1
21.0	20.4	5.69 ± 0.06	8.0 ± 1

* The ratio of the He content of the sample to that of London air.

each value in the third column is the mean of three determinations of helium in the given sample.

Paneth and Glückauf concluded from these results that the gravitational separation of gases already begins to make itself felt at an altitude of 21 km. They considered that the results obtained previously by Lepape and Colange were in good agreement with theirs, and also confirmed the presence of the level of gravitational separation somewhere around 20 km above the Earth's surface.

Further work on the determination of the composition of samples of air taken from high altitudes was done by Regener in Germany, in 1935–1936 /68, 69/. He carried out a whole series of carefully thought-out measurements. In this investigation, the balloons carrying the sampling bulbs reached record altitudes of 28–29 km. Regener managed to get his bulbs to such high altitudes by using a number of balloons joined together (and not just one, as normal) for carrying each bulb (see Figure 10), so that the height could be increased without reducing the load-carrying capacity. Moreover, he used very good quality balloons, selected from a large batch. The altitude reached by the bulb was determined by a special electrical aneroid barometer. In order to guarantee the reliability of the results, the balloons were separated from the bulb by a distance of 20–40 m, so that an incredibly large amount of hydrogen would have to escape from the balloons

* More details of the sampling technique are given on p. 46

to affect the analysis of the samples. Regener analyzed his samples for oxygen. The glass sampling vessel is shown in Figure 11. It consisted of two bulbs (a large one of capacity 3 liters and a small one of capacity 100 cm^3) connected together. The vessel was provided with an ordinary vacuum tap to let the air from the stratosphere into the evacuated bulb. This tap was operated automatically by means of an electromagnetic device shown in Figure 11.

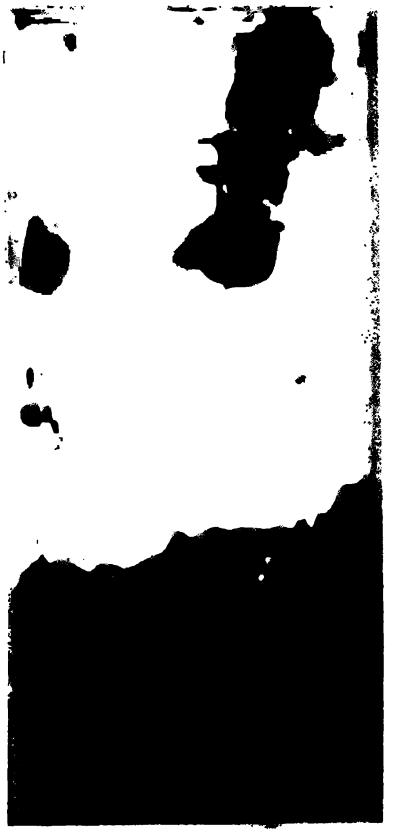


FIGURE 10. A string of sounding balloons for lifting the sampling vessel

The use of a vacuum tap instead of the usual capillary inlet (which had to be broken and then sealed by melting or some special cement) considerably increased the reliability of the experiments but also introduced its own difficulties. The tap was lubricated with vacuum grease, which, as was found out some time later, could absorb oxygen from the air sample. The grease also led to another difficulty: its prolonged stay in the stratosphere made it freeze, after which it was naturally very difficult to turn the tap. In order to keep out the extreme cold, the bulb and the tap were wrapped in cellophane, while a sheet of thin aluminum foil was placed under the bulb to reflect the sunlight. The sunlight was reflected onto the tap and

warmed it up slightly. To prevent the tap freezing up, it was also surrounded by a small electric heating coil which could be used to supply extra heat if necessary.

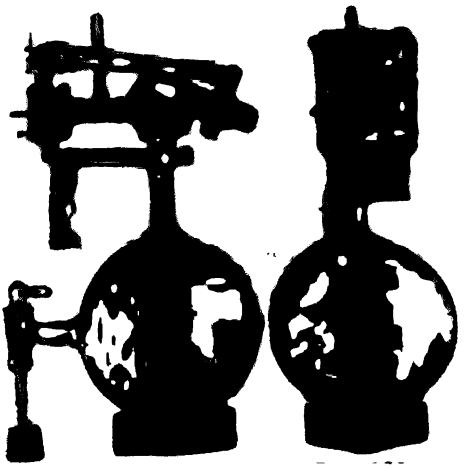


FIGURE 11. The air-sampling vessel used by Regener for his sounding-balloon investigations

One great step forward compared to other similar investigations was the special construction of the sampling vessel; this construction allowed Regener to carry out the analysis of the sample inside the vessel itself. This removed the necessity of transferring the sample to another container for analysis, during which process there was always a great risk that the sample would be contaminated or part of it lost.

The air samples were analyzed as follows. On arrival in the laboratory the vessel containing the sample was connected via the tap H (Figure 12) with the reservoir D, filled with mercury, which was in its turn connected to a manometer. In order ensure the constancy of all the measured volumes, the sampling vessel and the manometer were placed in a thermostatically controlled water bath. The mercury from the reservoir D was then admitted into the large bulb V_2, forcing the air into the small bulb V_1. The mercury was allowed to rise to a strictly determined level in the bulb, marked by a Jolly line B sealed into the bulb. The mercury level p_1 in the manometer C was then read by means of a catherometer to within an accuracy of 0.001 mm. The water was next drained out of the water bath, and the side arm A of the small bulb (which contained copper) was heated with a gas burner. The copper was heated to red heat for 20 — 40 minutes, thus removing all the oxygen from the sample. The water bath was then refilled with water at the same temperature, and the mercury readjusted to the same level. Knowing the volume of the small bulb, measurement of the new mercury level in the manometer gave the oxygen content of the sample. The results obtained by Regener in this way are shown in Table 17.

As can be seen from Table 17, the oxygen content remains nearly constant up to an altitude of 18–20 km, after which there is a noticeable decrease in the oxygen content with height: at an altitude of 28 km, this decrease amounts to 2–3 %.

Regener compared his results with those of Lepape and Colange* on helium, and found reasonable agreement (an increase of 8 % in the He content corresponds to a decrease in the O_2 content of 1.5 % at an altitude of

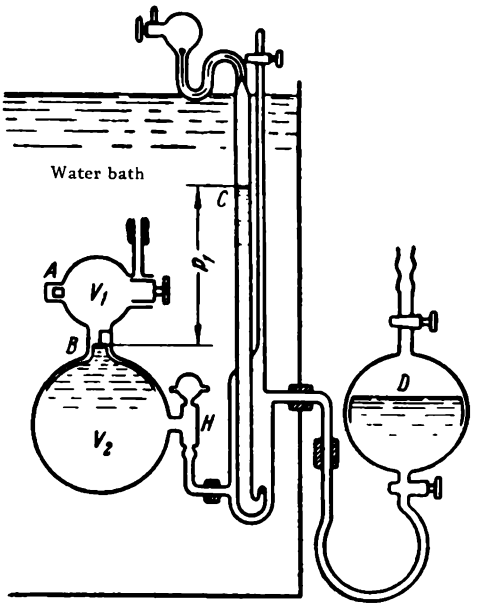


FIGURE 12. Regener's apparatus for analyzing the air samples

23 km). Regener, like Lepape and Colange* for helium, found a considerable fluctuation in the oxygen content at different heights. He explained this as being due to the different heights of the stratosphere above the equator and the poles. As a result of this the more abundant oxygen in the equatorial air** falls towards the polar regions, giving rise to the observed fluctuations. Regener's careful experiments thus gave a height of 20-21 km as

TABLE 17

Date	Pressure of sample, mm Hg	Height of sampling, km	O_2 content, %
24 August 1936	621.5	0	20.93 ± 0.02
19 December 1935	109	14.5	20.89 ± 0.05
5 December 1935	47	18.5	20.84 ± 0.02
18 July 1936	62	18.5	20.88 ± 0.02
5 February 1935	28	22.2	20.57 ± 0.05
12 February 1936	19	24	20.74 ± 0.02
6 May 1936	6.3	28-29	20.39 ± 0.05

the lower limit of gravitational separation. Since the determination of oxygen was at the limits of experimental accuracy, we should also consider the trouble involved in the determination of oxygen in the sample.

* [Paneth and Glückauf probably meant.]

** It is more abundant in the sense that a given height will be a different distance from the level of gravitational separation at the equator and at the poles.

Some time after Regener, Paneth and Glückauf carried out a new investigation of the air at high altitudes /70, 71/, using an apparatus designed by Dines /72/. This apparatus (Figure 13) consisted of a bulb, about

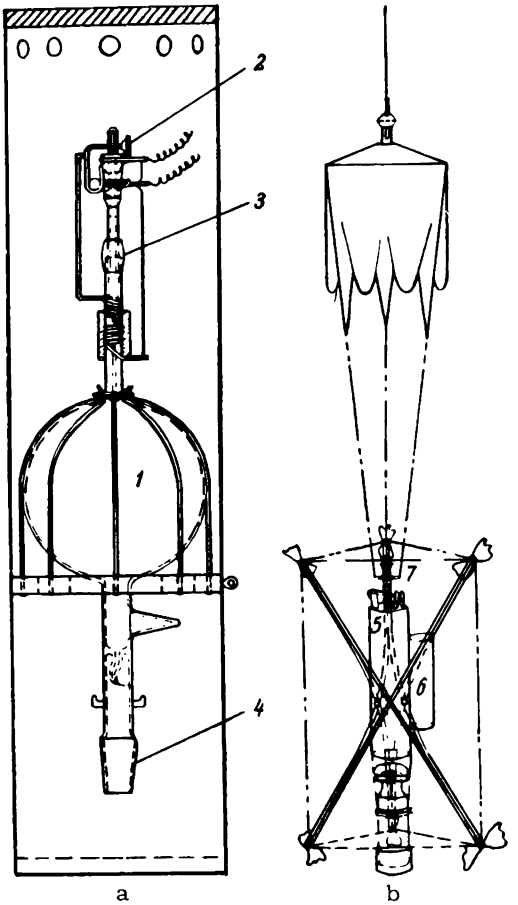


FIGURE 13. Dines' apparatus for the investigation of air at high altitudes

a–Dines' bulb in cardboard cylinder: 1–body of bulb; 2–system for opening bulb; 3–system for closing bulb after sampling; 4–ground joint for connecting bulb to analytical apparatus; b–sketch of apparatus in use: 5–cylinder with bulb; 6–Dines' barograph; 7–spring.

500 cm^3 capacity, carried by a sounding balloon. Figure 13a shows such a bulb, mounted in a cardboard cylinder and fitted with opening and closing devices. Figure 13b shows a sketch of the whole apparatus during the ascent. Dines' barograph (cylinder 6) was joined to the cardboard cylinder 5 containing the evacuated glass bulb. Both cylinders were mounted in a light bamboo frame, which protected the bulb during the return to Earth. This frame was fastened by means of the spring 7 to the ascending balloon.

The sampling was not begun until the balloon had reached its maximum height, burst, and the parachute had opened. The mechanism for opening the bulb is shown in Figure 14. On the thin-walled capillary 1 of the sampling bulb is fitted a wooden cap 2, on which is mounted the spring 3. This

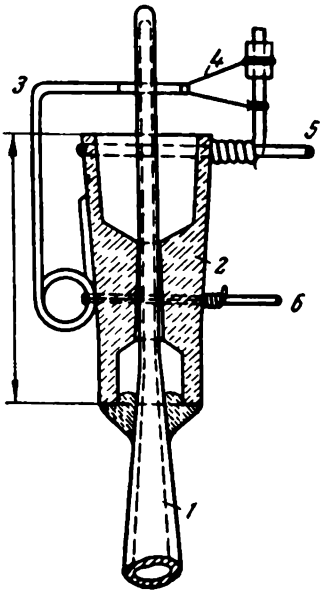


FIGURE 14. Diagram of system for opening Dines' bulb

spring ends in a ring through which the end of the capillary passes, and is kept in a state of tension by the wire 4. Current from a battery is supplied to terminal 5 via a switch (mounted in spring 7, Figure 13). This current is turned on the moment the parachute opens, burning through the wire 4. The spring is thus released and returns to its equilibrium position, breaking the thin-walled capillary in the process. The bulb is thus filled with air. At this moment, the barograph makes a mark and thus records the value of the pressure. This allows the height of sampling to be determined, and also serves as a check on the proper functioning of the sampling mechanism: if the pressure inside the bulb is equal to that recorded by the barograph, the sampling mechanism is working properly. After the sample has been taken, the bulb is closed by means of the sealing device (3 in Figure 13). A narrow part of the inlet tube is filled with liquid picein, which solidifies to a tight-fitting plug. A narrow hole (diameter 1 mm) is made through this plug. A platinum heating coil is wound around the tube at the spot where this plug is situated, and is turned on for 15-20 seconds after the bulb has been filled, thus melting the picein enough to seal the bulb effectively. The weakness of this design (the melting of the picein, which might contaminate the incoming air) did not have much effect, since Paneth and Glückauf analyzed the samples for helium, which is neither absorbed nor evolved by molten picein. The lower part of the bulb was provided with a ground joint for connecting the bulb to the vacuum apparatus in which the gas analysis was carried out. Dines' bulbs were carried up to altitudes of 20-25 km, and allowed the air at these heights to be analyzed for helium. The experimental

results, together with those from previous investigations, are shown in Table 18, which is taken from a paper by Paneth /73/.

TABLE 18

Height, km	He*		O_2	
	content, 10^{-4}% by volume	deviation from content near Earth, %	content, % by volume	deviation from content near Earth, %
0	5.240	0	20.945**	0
			20.92***	0
9–17	–	–	20.92****	0
14.5	–	–	20.89***	–0.14
16.5	5.27	0.5	–	–
18.0	5.26	0.4	–	–
			20.95*****	0
18.5	5.28	0.7	20.84***	–0.38
19.0	5.27	0.5	20.87	–0.24
21.0	5.64	7.0	–	–
21.5	–	–	20.895**	–0.24
	5.45	4.1		
22	5.35	2.0	20.57***	–1.7
22.5	5.51	5.1	–	–
	5.34	1.9		
23.5	5.46	4.2		
	5.27	0.5	–	–
24	–	–	20.74***	–0.86
25	5.35	2.1	–	–
28–29	–	–	20.39***	–2.5

* Gluckauf and Paneth; ** Shepherd; *** Regener; ****Lepape and Colange; ***** Moskvin and Cherepennikov.

This table summarizes practically all the work performed on the analysis of air from high altitudes starting with the ascent of the stratosphere balloon "SSSR" and ending with the work of Paneth and Glückauf in 1937-1938. Careful inspection of this table will show that there is a noticeable increase in the concentration of the light gas (helium), and a decrease in that of the heavy gas (oxygen) starting from an altitude of 20 km. However, as pointed out by Paneth, these variations in the helium and oxygen contents are not quantitatively in accordance with the law of gravitational separation of gases. Paneth therefore concluded that the mixing of the atmosphere continued up to an altitude of 20 km and more, causing the composition of the air to differ from that which would be found if purely gravitational separation of gases prevailed. However, Paneth assumed that the gravitational separation of gases began somewhere between 20 and 30 km above the Earth.

This work of Paneth formed the close of the investigation of the composition of the air at high altitudes by means of balloons. On the basis of the results quoted above, the investigators formed the impression that gravitational separation of gases in the atmosphere begins at an altitude of about 30 km above the Earth's surface.

Conclusion

For nearly one and a half centuries scientists have been analyzing the air at different heights, looking for the lower limit of the gravitational separation of gases.

The first narrow aim of these investigations (confirmation of Dalton's law) gradually gave way to an interest in the nature of the upper atmosphere for its own sake. As we have already mentioned (see Preface), an accurate knowledge of the composition of the atmosphere is necessary for the solution of many other problems of the upper atmosphere, which continually spurred scientists to carry out new investigations in this field. If we look at the course taken by these investigations, begun by Dalton and still a long way from finished 140 years later, we can clearly discern a continuous improvement in the experimental methods and techniques used, and a gradual change in the ideas about the structure and composition of the atmosphere at high altitudes. Of course, it is difficult to compare the original samples, taken by Dalton in ordinary bottles in 1803, with the refined methods of automatic sampling developed by Paneth for his sounding-balloon experiments in 1939; it is equally difficult to compare the methods of analysis. Our knowledge in this field has greatly increased since the first attempts to determine the composition of air, yet the problem of the height at which the gravitational separation of gases begins still evades solution. However, this certainly does not mean that no progress has been made in the determination of the chemical composition of the atmosphere: on the contrary, the progress has been enormous and of great value to geophysics. But the problem as to the extent of the region of thorough mixing of the atmosphere still remains. Each new investigation of the composition of the air raised the height of this region further and further: it was found that even the lower boundary of the stratosphere did not act as a barrier to the mixing of the atmosphere, so that even at the highest altitudes reached, i. e., 20-30 km, Dalton's law was still far from being obeyed.

It is interesting to see how in this process the limit of gravitational separation was continually "found" and then "lost" again. If we look carefully at the material contained in this chapter, we can see how right from the start investigators have claimed to have discovered the long-sought-after limit of gravitational separation somewhere near the maximum height reached by them, only to have their claim refuted by new experiments at higher altitudes, while the elusive limit of gravitational separation seemed to remain continually just out of reach. For example, Dalton thought that he had found this level at an altitude of 3 km, while Gay-Lussac, taking samples from an altitude of 7000 m, found no change of composition; then Welsh took samples at about 6000 m and found some decrease in the oxygen content, but Cailletet and Teisserenc de Bort failed to find any such effect even higher altitudes. Tetens and Wigand found an increase in the content of light gases at altitudes round about 8 km. Then the lower boundary of the stratosphere was suggested as the limit of gravitational separation, but the stratosphere balloon "SSSR", ascending far beyond this level, disproved this too: the composition of the atmosphere at an altitude of 18.5 km was found to be identical with that at the Earth's surface, and so on.

The end of the investigation of the composition of the atmosphere with the aid of balloons saw the limit of gravitational separation of gases "fixed" at about 30 km above the Earth (Paneth, 1939).

Alongside the increase in the height of the investigations, a great change can be observed in both the qualitative and quantitative aspects of the methods which were used to analyze the samples. The rapid decrease in the amount of gas brought back from higher altitudes, and the high demands made on the experimental accuracy, forced the investigators to work out painstakingly accurate microanalytical methods to enable them to analyze a few cubic centimeters of air (at N.T.P.) for the gases in question (helium, argon, oxygen, nitrogen). Paneth's last work in this field may be regarded as an ideal example of physicochemical methods of microanalysis of gaseous mixtures.

Finally, as the height of the investigations increased, the method of sampling was gradually improved. While the first bottles of "mountain air" were sealed with a simple cork, immeasurably higher demands are now made on the purity of the air sealed in the sampling vessels, and on the cleanness of the sampling vessels themselves. The necessity of automizing all operations involved in opening and closing the sampling vessels made many further demands on the experimenter.

The improvements in sampling methods, microanalytical technique and range of the sampling devices which we have described led to the results summarized in Table 18. These results led most investigators to believe that the limit of gravitational separation of gases was situated an at altitude of about 30 km. However, in order to give a complete picture of the state of opinion on the question of the composition of the atmosphere at high altitudes up to the beginning of the Second World War, we must include a brief resumé of the results of the indirect investigations in this region of the atmosphere. We would like to end this chapter with a summary of the words written, also in 1939, by the great geophysicist Sidney Chapman on this subject /74/.

Discussing the latest results obtained by Paneth on the increase in the content of light gases with height, Chapman remarked that even if such an increase was found at 20-30 km it could not continue into the higher regions of the atmosphere since neither the spectra of the polar aurora nor those of the night airglow showed any traces of helium or hydrogen. On the other hand, these spectra were rich in molecular oxygen and nitrogen bands, showing that these gases are still important constituents of the atmosphere at high altitudes. It is quite possible that the light gases, hydrogen and helium, diffuse into outer space from the upper atmosphere because of the high temperatures there.

It is very interesting that the spectra of the polar aurora and of the night sky contain intense lines due to atomic oxygen. This shows that oxygen dissociates at heights of about 100 km. This dissociation is due to ultraviolet radiation from the Sun, with $\lambda < 1500$ Å.

In conclusion, Chapman put forward the idea that the chemistry of the upper atmosphere is the chemistry of oxygen and nitrogen, with variations in the concentrations of the different forms of oxygen. Thus, the difference between the views of investigators using direct and indirect methods of investigation continued right up to the end of the period under discussion, and was only resolved by the new work which we shall describe in the next chapter.

Chapter III

INVESTIGATIONS OF THE COMPOSITION OF THE UPPER ATMOSPHERE USING ROCKETS
(Sampling method)

Introduction

In the previous chapter we have described in detail the investigations of the composition of the air at various altitudes up to 30 km, in which region sounding balloons are capable of carrying the automatic bulbs used for air sampling. The results of these investigations did not allow definite conclusions to be drawn about the level of gravitational separation of gases. It was thus necessary to carry out new investigations at considerably higher altitudes. However, the existing means of ascending to high altitudes had more or less been exhausted: the rapid decrease of pressure with height (Figure 15) placed a limit on such experiments. It might be possible to raise the ceiling of the sounding balloons by a few kilometers; but theoretical calculations had shown that one could not hope to find the level of gravitational separation below about 100 km.

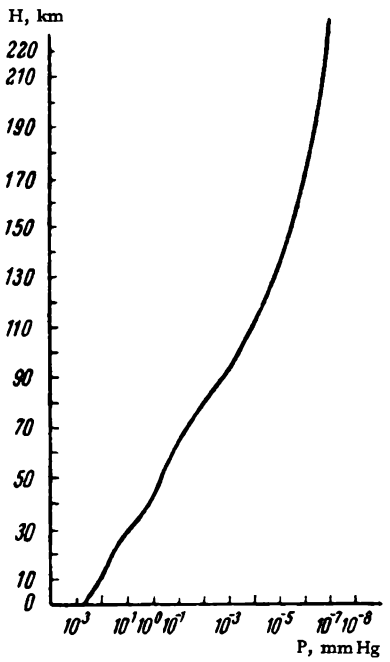


FIGURE 15. Atmospheric pressure as a function of height

We shall now give a brief account of the considerations which led to this conclusion.

Any gas in the Earth's atmosphere is distributed at various heights according to the known barometric law:

$$\rho_z = \rho_0 e^{-\frac{mgz}{RT}}, \qquad (1)$$

where ρ_z is the density of gas at height z, ρ_0 is the density of gas at the Earth's surface, R is the gas constant, T is the absolute temperature, g is the gravitational constant [sic] and m is the mass of one mole of the gas. The partial pressure p of the gas varies according to a similar law.

If the atmosphere were isothermal we could calculate the pressure of any given gas at various distances from the surface of the Earth using the barometric formula. The calculation becomes rather more complicated if we take into account the variation of temperature with height (Figure 16).

According to the barometric formula, the distribution of a gas with height depends on its molecular weight: the heavier a gas is, the more rapidly its density (and its partial pressure) decreases with height.

If we also take into consideration that according to Dalton's law each gas in a gaseous mixture (as long as it does not react with other gases) behaves as if the other gases were not present, then it follows that each component of a gaseous mixture in the gravitational field of the Earth is distributed according to the barometric formula, independent of all the other gases.

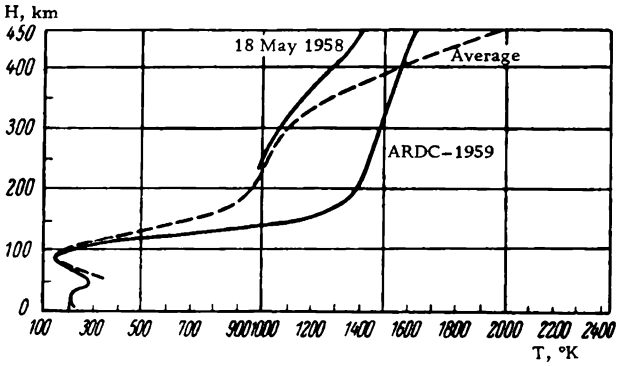


FIGURE 16. Variation of temperature with height

The above argument would indicate that the upper atmosphere should consist mainly of light gases. However, mixing processes equalize the gaseous composition of the atmosphere up to a considerable height. We can determine this height by comparing the time needed to mix the atmosphere with the time needed for the atmosphere, once mixed, to return to gravitational equilibrium. The level of gravitational separation will then be that height at which the mixing time begins to exceed the time for reaching gravitational equilibrium.

We shall now show how the time of gravitational separation can be calculated, as described in the literature /30/.

We suppose to begin with that two gases with concentrations n' and n'' are completely mixed. Let $(N'_z)_{D\uparrow}$ be the number of molecules of the first gas diffusing upwards through unit (horizontal) area per unit time at height z. Then

$$(N'_z)_{D\uparrow} = -D\frac{\partial n'_z}{\partial z}$$

where D is the diffusion coefficient*. At the same time, part of the molecules of the first gas will descend under the influence of gravity, the number per unit area and unit time being given by

$$(N'_z)_{g\downarrow} = v_1 \cdot n'_z,$$

* The diffusion coefficient is given by

$$D = \frac{1.34}{3}\,\frac{n'_z\lambda''_z\vec{v}'' + n''_z\lambda'_z\vec{v}'}{n'_z + n''_z},$$

where λ'_z and λ''_z are the mean free paths of molecules of the first and second gases at height z, and v' and v'' are the mean velocities of these molecules.

where v_1 is the effective velocity of descent of the molecules. The net rate of passage of the molecules of this gas upwards is thus given by

$$(N_z')_\uparrow = -D\frac{\partial n_z'}{\partial z} - v_1 n_z'. \tag{2}$$

If equation (2) is to apply under the conditions found in the real atmosphere at heights exceeding 80 km, the increase in temperature with height occurring in this region must be taken into account. To a first approximation, the temperature increase may be taken to be linear; the concentration of molecules will then vary with height as follows:

$$n_z' = n_0'\left(\frac{T}{T_0}\right)^{-\left(1+\frac{m'g}{\alpha k}\right)}, \tag{3}$$

where α is the temperature gradient, m' is the molecular weight of gas in question, g is the acceleration due to gravity and k is the Boltzmann's constant.

Let us now determine v_1, occurring in equation (2). This may be done by putting $(N_z')_\uparrow = 0$, using the values of n_z' and $\frac{\partial n_z'}{\partial z}$ from equation (3):

$$v_1 = D\frac{m'g + k\alpha}{kT}. \tag{4}$$

If we insert this value of v_1 in equation (2), we obtain

$$(N_z')_\uparrow = -D\left(\frac{\partial n_z'}{\partial z} + \frac{m'g + k\alpha}{kT} n_z'\right). \tag{5}$$

The variation of $(N_z')_\uparrow$ must thus be very complicated, depending as it does on the variables n_z', n_z'', λ_z', λ_z'', $\frac{\partial n_z'}{\partial z}$ and $\frac{\partial n_z''}{\partial z}$. The author of the work cited above overcame this difficulty by assuming that these variables are exponential functions of a quantity η, the degree of gravitational separation*, i. e.,

$$(n_z')_\eta = (n_z')_{\eta=0} \cdot e^{-\beta'\eta},$$

$$\left(\frac{\partial n_z'}{\partial z}\right)_\eta = \left(\frac{\partial n_z'}{\partial z}\right)_{\eta=0} \cdot e^{-\vartheta'\eta}.$$

Similar equations are obtained for the second gas in the mixture.

The constants β', β'', ϑ' and ϑ'' are determined from the fact that η varies from zero for pure diffusion to unity for complete separation. Once these constants have been determined, we can calculate n_z', n_z'', λ_z', λ_z'', $\frac{\partial n_z'}{\partial z}$ and $\frac{\partial n_z''}{\partial z}$, and hence the rate of gravitational separation at each stage of the diffusion process. The time needed for a certain degree of gravitational separation can then be found by graphical integration.

Calculations carried out by Mitra and Rakshit /104/, and also by Epstein /103/, showed that at a height of about 100 km the mixing time is much less than the time required for establishing gravitational separation (which at lower levels is measured in years). Taking 100 km as the lower limit of the level of gravitational separation, Mitra and Rakshit calculated the time

* The parameter η is equal to the ratio of the number of molecules of gas (1) or (2) which have passed upwards to the total number which must pass upwards before gravitational separation is complete.

needed for the separation of gases at different heights. The results of these calculations are given in Table 19.

TABLE 19

Height, km	Time needed for 80% gravitational separation, hours			Height, km	Degree of gravitational separation after 10 hours, %	
	N_2, O	N_2, O_2	N_2, O_2		N_2, O	N_2, O_2
	T increasing		T const		T increasing	
165	–	–	14.12	100	0	0
175	–	68.26	5.53	125	3.5	2.5
200	–	–	0.46	150	10.5	9
225	–	10.09		200	43	47
250	17.47	3.90		250	71	95
300	7.98			300	82	100
350	3.67			350	91	–
				400	100	–

It can be seen that even when "left in peace", a mixed atmosphere reaches gravitational equilibrium rather slowly under the influence of gravitational forces and diffusion. Under real conditions, taking mixing processes into account, the establishment of equilibrium will only be possible at altitudes higher than 100 km. It is true that these calculations are not very accurate, and that the level of gravitational separation may in fact lie considerably lower, say at heights of 50–70 km. However, even in this case experiments would have to be carried out at considerably higher altitudes in order to obtain positive evidence of the separation of gases such as nitrogen and oxygen; just above the level of gravitational separation, the separation process would be very slow and enormously difficult to measure. This may be shown by the following example*.

Let us write the barometric formula in the form

$$p = p_0 \cdot e^{-\frac{z}{H}}, \tag{6}$$

where $H = \frac{RT}{mg}$.

The variation of the number of molecules per unit volume (concentration) can be expressed by a similar formula:

$$n = n_0 \cdot e^{-\frac{z}{H}}. \tag{7}$$

Let us further denote the ratio of the concentrations n and n' of two gases of molecular weight m and m' at a height z by γ, i. e.,

$$\gamma = \frac{n}{n'}.$$

Since equation (7) holds for both gases, it follows that

$$\gamma = \frac{n}{n'} = \frac{n_0}{n_0'} e^{-\left(\frac{z}{H} - \frac{z}{H'}\right)} = \gamma_0 e^{-\frac{z}{H_1}},$$

* Taken from reference /81/

where $H_1 = \frac{RT}{(m' - m)g}$ and $\gamma_0 = \frac{n_0}{n_0'}$ is the ratio of the concentrations of the two gases at the Earth's surface.

The gravitational separation of the gases may be characterized by the quantity

$$Q = \left(\frac{\gamma'}{\gamma_0'} - \frac{\gamma}{\gamma_0}\right), \tag{8}$$

where γ' and γ_0' are the corresponding ratios of the concentrations of the two gases in a completely mixed atmosphere. Naturally, in a completely mixed atmosphere $\gamma' = \gamma_0'$. Therefore, equation (8) becomes

$$Q = 1 - \frac{\gamma}{\gamma_0}.$$

Making use of the above expression for γ and γ_0 and multiplying by 100, we obtain an expression for the percentage gravitational separation of the two gases in question at different heights,

$$Q = (1 - e^{-\frac{z}{H_1}}) \cdot 100. \tag{9}$$

Values of Q calculated with the aid of equation (9) are given in Table 20. These figures indicate the gravitational separation of various gases which would be found at various heights above the level at which separation begins, if mixing processes were completely absent from the Earth's atmosphere.

TABLE 20

Height, km	Q, %			
	N_2/O_2	O/N_2	He/N_2	H_2/N_2
1	1.9	5.0	9.6	10.4
3	4.6	14.0	26.2	28.0
5	9.3	22.4	39.6	42.2
8	14.5	33.3	55.4	58.4
15	25.5	53.2	78.0	80.7
25	38.8	71.8	92.0	93.0
50	62.5	92.1	99.4	96.6
100	85.9	99.4	–	–
200	92.0	–	–	–

As can be seen from Table 20, the separation of the two most important gases in the atmosphere (oxygen and nitrogen) is particularly small.

Matters are further complicated for the investigator by the fact that the division between the region of mixing and the region of separation is not sharply defined. There is an extended transition region, in which mixing processes still have a considerable influence alongside the gravitational separation. In this region, the separation of the light gases from the heavy ones will proceed even more slowly than indicated in Table 20.

Such in brief were the theoretical conclusions about mixing in the atmosphere. What was now wanted was rigorous experimental verification of these conclusions.

The practical problem of finding the boundary of gravitational separation was very complex. At high altitudes (above 60 km), atmospheric gases (in

particular oxygen) dissociate into atoms under the influence of ultraviolet, particulate and X-radiation from the Sun; and these atoms enter into chemical reaction with other atoms or molecules. This naturally complicates the distribution of gases at various heights even more.

The presence of photochemical reactions in the upper atmosphere gives rise to a dynamic equilibrium, which is shifted by changes in the degree of exposure to the Sun's radiation and in solar activity. These circumstances demanded that experiments be carried out at altitudes which had never yet been attained by measuring equipment. Such altitudes were only accessible to rockets.

At the end of the 1930's and the beginning of the 1940's rocket techniques were still in their infancy, and could not even be relied upon for reaching altitudes attainable by sounding balloon. Direct investigations of the upper atmosphere were slowed down very considerably at this time, and the outbreak of the Second World War put a general stop to investigations on the composition of the upper atmosphere by direct methods for nearly a decade.

The rapid advances in rocket techniques from 1940–1946 provided the conditions necessary for a resumption of the interrupted work on the direct investigation of the upper atmosphere. In the middle of 1946 the first rocket carrying scientific equipment reached an altitude of 70 km; science had acquired a powerful new tool for probing the atmosphere at high altitudes.

1. Gaseous composition — one of the central problems of the physics of the upper atmosphere

In the years after the war, scientists began an intensive study of the upper atmosphere using rockets. Among these investigations, the determination of the gaseous composition occupied a special place.

In the lower atmosphere, where the mean free path of the molecules is much less than the linear dimensions of the measuring equipment, the measuring equipment itself has no significant effect on the determination of such atmospheric parameters as pressure, temperature, density, composition, etc.* Matters are different in the upper atmosphere. Here the mean free path of the molecules is comparable to, or even considerably greater than, the characteristic dimensions of the measuring equipment. Moreover, the upper atmosphere is constantly under the powerful influence of shortwave ultraviolet, particle and X-radiation from the Sun, which give rise to various photochemical and ionization processes in these regions. This leads to considerable changes in the composition and other properties of the atmosphere. This is a very strange region of the atmosphere, according to our "earthly" conceptions. The interdependence of different phenomena is so considerable that it is senseless to carry out an investigation on one parameter of the upper atmosphere without considering the others. Because of this, the solution of the problem of the composition of the upper atmosphere has constituted the key to the solution of other problems of the upper atmosphere which at first sight would seem to be independent of the composition. A few examples will make this clear.

The measurement of pressures in the upper atmosphere at present cannot be accurate because the manometers used for recording low pressure

* A few technical difficulties may arise, but they can all be solved.

(ionization, gas-discharge and thermal gauges) give a reading which depends considerably on the nature of the gas in which they are working /76/.

To an even greater extent than with the determination of the pressure, the determination of the temperature of these levels without a knowledge of their composition is impossible. As is well known /77/, it is impossible to determine directly the temperature at high altitudes by means of some device installed in a rocket. Because of this, the desired temperature is calculated on the basis of suitable data. The temperature is normally calculated from the barometric formula, starting from measured values of the pressure, but the pressure itself cannot be measured sufficiently accurately without a knowledge of the gaseous composition.

The problem of the dissipation of the atmosphere has not yet been solved finally. The problem of helium, for example, may be solved if we know the gaseous composition of the upper atmosphere from which the helium diffuses into interplanetary space.

The problem of the corpuscular radiation of the Sun will be elucidated if we manage to obtain reliable information about the gaseous composition of the atmosphere in the region of the polar aurorae at the moment of their maximum intensity: it is very likely that an increase in the hydrogen content of the atmosphere will be found just here.

There are still other unsolved problems connected with the investigation of the ionosphere. For example, our knowledge of the nature of the ionized particles in this region is quite insufficient. This knowledge is extremely important, as it may be very useful in solving a series of problems to do with the genesis and nature of the ionosphere on the one hand and with the determination of some of its electrical parameters on the other. Finally, the problem of finding the level of gravitational separation of gases remains as important as ever.

Apart from these problems of a purely scientific nature, a knowledge of the composition of the upper atmosphere is very important for practical calculation of the trajectories of rockets and artificial satellites.

The examples given above, though by no means exhaustive, are nevertheless sufficient to give some idea of the central position which should be assigned to the investigation of the composition of the upper atmosphere.

2. Sounding rockets

At the present, only a few countries are carrying out investigations of the upper atmosphere using rockets. The leading role in these investigations is played by the USSR and USA, while France, England and Japan are also doing some work.

Soviet scientists use various types of rockets for probing the upper atmosphere. These are capable of carrying scientific equipment to widely differing altitudes. The enormous power of the Soviet geophysical rockets allows loads of over one ton to be carried to altitudes of about 500 km: such a rocket has in fact reached an altitude of 475 km, which is a record for a single-stage rocket. Owing to the high lifting-capacity of the geophysical rockets special automatic containers can be used for investigating the physical parameters of the atmosphere. These containers, which will be described in the next chapter, are shot out of the rocket by means of mortars and contain measuring equipment (including bulbs for sampling the air and

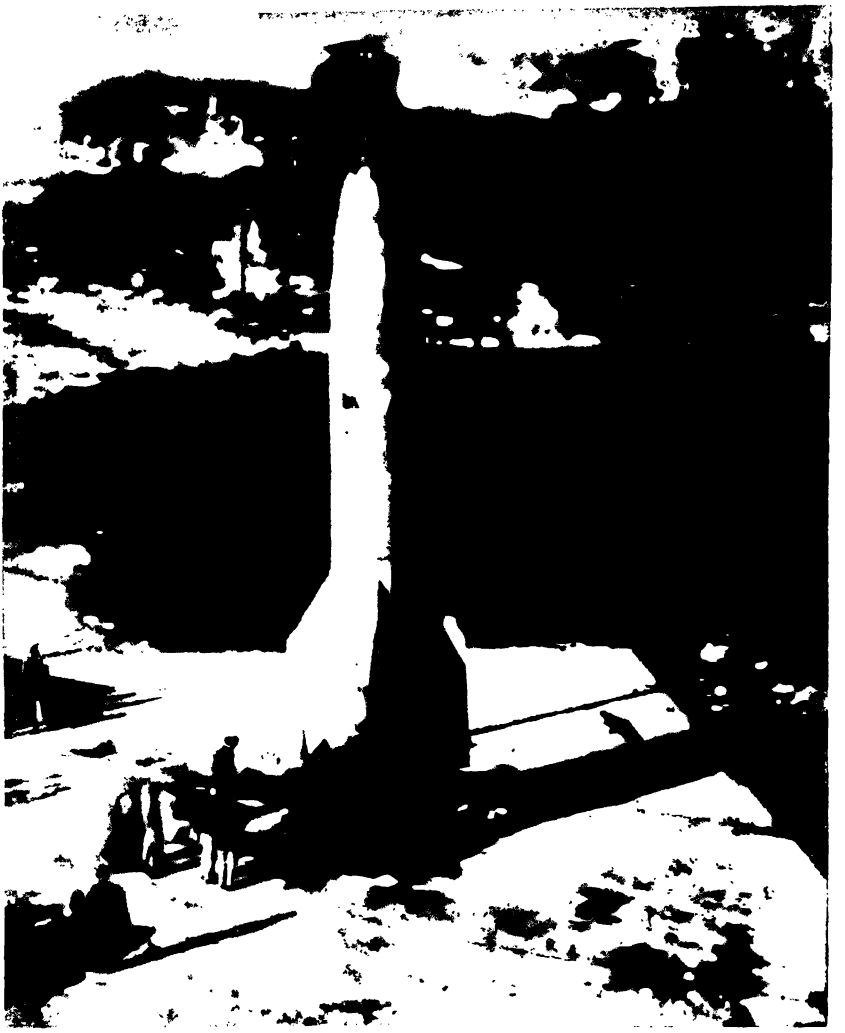


FIGURE 17. A V-2 rocket on the launching pad

radio-frequency mass-spectrometers). Ejecting the container from the rocket ensures that the experiments are carried out in much cleaner conditions than in the rocket. The carrying out of experiments away from the rocket is a much better method for investigating the upper atmosphere than taking measurements in the rocket itself, as is done outside the USSR.

Meteorological rockets are used in the Soviet Union for carrying scientific apparatus to lower altitudes. In this case the measuring equipment is contained in the nose of the rocket, and the rocket returns to Earth by parachute.

The rockets used outside the USSR for scientific purposes are not nearly as powerful as the Soviet geophysical rockets. Naturally, this severely limits the experiments which can be carried out with them.

FIGURE 18. The "WAC Corporal"

The USA uses a number of different models of rockets for these investigations, but none of them has reached a height of more than 300 km, despite the fact that the load of scientific equipment did not exceed a few hundred kilograms. The first rockets used in the USA for probing the atmosphere were modernized German "V-2" rockets, seized by the American forces after the end of the Second World War. These rockets, weighing 14 tons and 15 m long, carried a payload of half a ton to altitudes of about 100 km (Figure 17).

At the same time as the V-2 ascents, a smaller rocket, the "WAC Corporal" was under development in the USA; this weighed 300 kg, and could carry a payload of 10 kg to an altitude of 65 km. The dimensions of this rocket were no more than: length 5.3 m and diameter 30 cm (Figure 18).

Because of its low payload capacity and relatively low ceiling, this rocket was not used very widely, though it was tried as a second stage to the V-2.

a

b

FIGURE 19. The "Aerobee-Hi"

a–the rocket in the laboratory (in the assembly shop); b–the rocket taking off from the launching tower.

This combination, called the "Bumper", reached the highest altitude of any rocket outside the USSR — 389 km. However, the production of these systems was discontinued because of their great unreliability and high costs.

The "Aerobee", a modification of the "Corporal", proved to be a more successful type of light rocket. It could carry a payload of 55 kg to an altitude of 100–140 km. The relatively low cost and high ceiling of the "Aerobee" made it a fairly popular rocket for experimental purposes (Figure 19). This rocket, like the Soviet meteorological rockets, could be launched not only from the ground but also from the deck of ships which were specially adapted for carrying out investigations far from land (Figure 20).

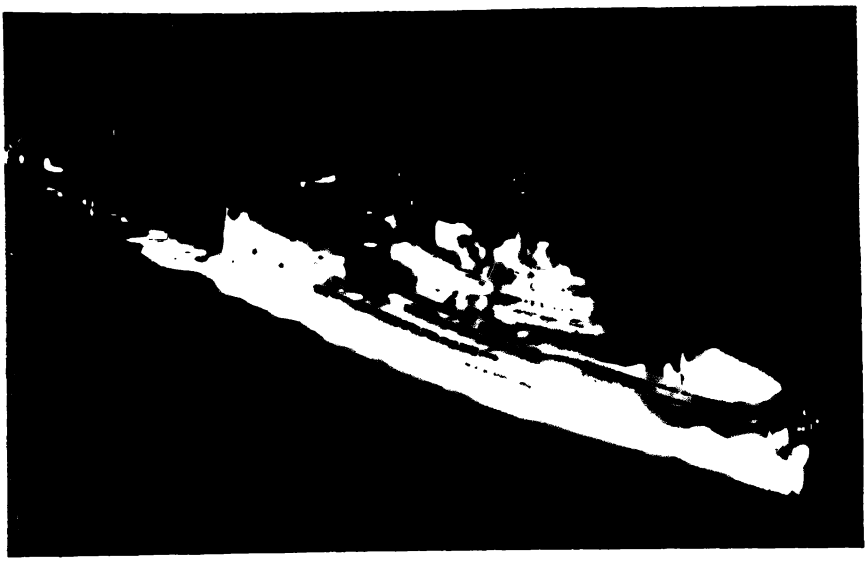


FIGURE 20. A ship fitted with a launching tower (at the stern) for an "Aerobee"–type rocket

The "Viking" rocket was another heavy one of the V-2 type, but with a considerably higher ceiling (Figure 21). The Viking was an experimental machine in both senses of the word: not only was it used for carrying out experiments, but its construction changed from flight to flight; it therefore had no fixed dimensions. We can however mention those of the "Viking-7" as an example: length 14 m, diameter 135 cm, weight 7.5 ton, payload 500 kg, ceiling 254 km (Viking-11)*.

The best research rocket in the USA can be considered to be the "Aerobee-Hi" (a modernized version of the Aerobee). The calculated ceiling of this rocket is 300 km, and in fact it has reached altitudes of 240–260 km, carrying 55–90 kg of scientific equipment.

England uses only one type of scientific rocket, the "Skylark". This rocket, which was only produced in 1957, can carry a load of 45–70 kg to an altitude of 160 km, and after modifications it has reached altitudes of 200–220 km.

* Production of "Viking" rockets has recently been discontinued.

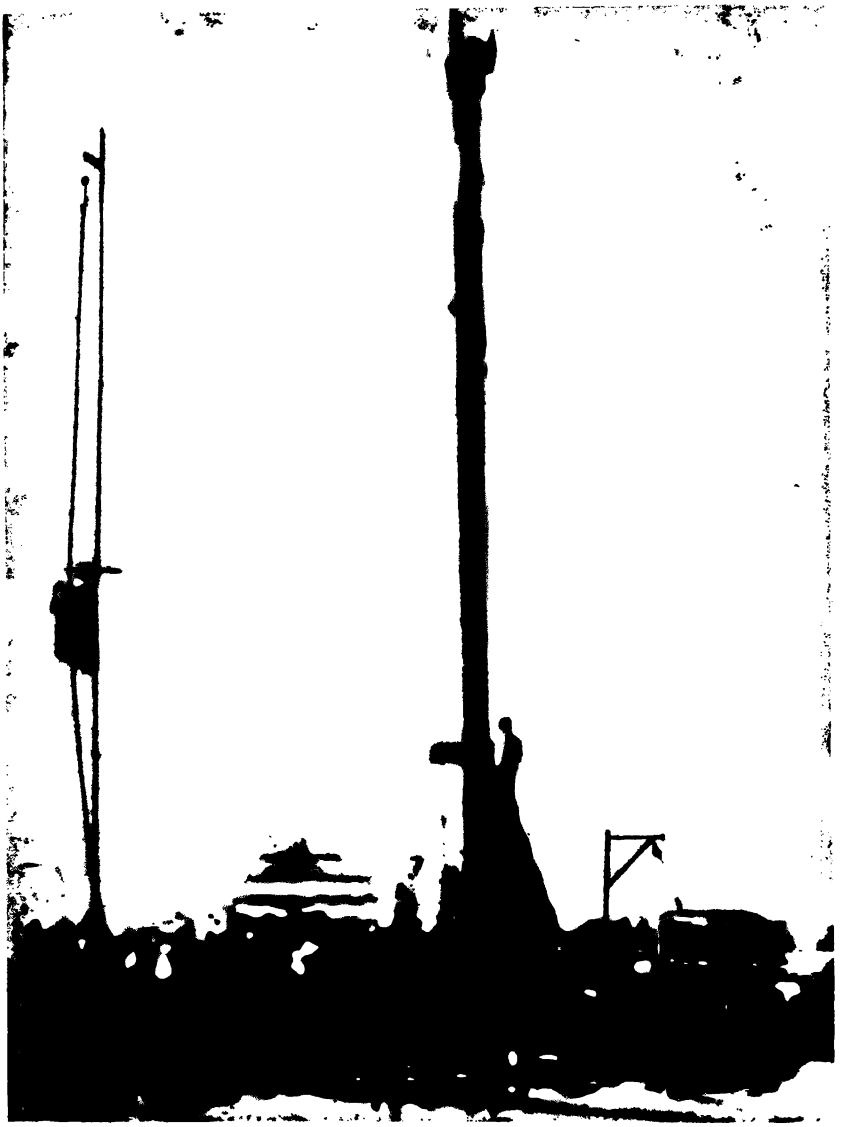


FIGURE 21. A "Viking" rocket ready for launching

In France, the "Veronique" rocket is used for scientific purposes; it can carry 40 kg to an altitude of about 100 km. About 30 of these rockets were launched in the Sahara in 1953–1954. At present, a new version, the "Super-Veronique" is being used. This can carry 45–75 kg to an altitude of 200 km.

The heavy rockets (V-2, Viking, Veronique, etc.), which have flight controls during acceleration, are launched straight from a launching pad.

The light rockets (Aerobee, Aerobee-Hi, WAC Corporal, etc.), having no controls, are launched with the aid of a gantry with guide rails (Figure 19b). In both cases, the rocket is accelerated for the first 30–50 km by its powerful motors (active part of the trajectory); the motors are then cut, and the rocket continues its flight in the gravitational field of the Earth.

During the ascent, most of the energy of the rocket motors is used up in overcoming the resistance of the dense layers of air near the Earth. Therefore, the higher the altitude of launching, the higher the rocket will climb with a given motor. This idea led to the combining of a rocket with a (Van Allen) sounding balloon, which proved very effective. This "Rockoon" (rocket-balloon) system was designed in the USA in 1956. It worked as follows. A small gunpowder-powered rocket, 2.7 m long, 16 cm in diameter and weighing 90 kg, was carried to a height of 20–25 km by an enormous nylon balloon (the "Skyhook"). The rocket was automatically ignited at this height, and had no difficulty in carrying a 20-kg load of instruments to altitudes of 100 km and more*. A certain amount of trouble is caused by the fact that the rocket takes about an hour to reach the stratosphere. During this time, it gets very cold, and this may prevent the measuring equipment working correctly. It is therefore necessary to take suitable precautions. The Rockoon system is very cheap (about thirty times as cheap as the Aerobee-Hi), and very mobile. Apart from the Rockoon, wide use is made of the "Rockaire" system, a combination of a rocket and an airplane.

Workers outside the USSR have used the V-2, Viking, Aerobee and Aerobee-Hi rockets for investigations of the composition of the atmosphere. We shall now proceed to describe this work, after a brief exposition of the main points where rocket investigations differ from investigations by other means.

3. Characteristics of rocket investigations

Scientific investigations carried out from rockets differ considerably from the sounding-balloon investigations which we have described above.

These differences are determined by three factors:

1) the enormous speed of the rockets, which may considerably exceed the speed of sound;

2) the free flight of the rocket, together with the scientific instruments, in the Earth's gravitational field;

3) the extreme rarefaction of the medium in which the investigations have to be carried out.

The space set aside for scientific equipment inside the rocket is an inconvienient and highly unusual "laboratory", in which special demands are made on the equipment. We shall now give some details of these demands.

1. Vacuum. All equipment and mechanisms placed in the rocket must work under conditions of high vacuum. This naturally makes special demands on the construction and operation of the equipment. It should be hermetically sealed, and as far as possible should not absorb or desorb gases. It should be stressed that the rocket, falling in the rarified atmosphere, begins to give off a cloud of "stray" gases: air which it absorbed near the Earth, combustion products, fuel fumes, etc. It is very important

* In recent years the payload and ceiling of the rocket carried up by the balloon have been considerably increased.

that these factors should be taken into account, and reduced to a minimum, if the experiments are to be carried out properly.

2. **Low inertia.** During its flight, the rocket achieves a velocity two-three times the speed of sound. Therefore, the equipment used to measure the various parameters of the atmosphere should be practically free from inertia. Only in this way can the data obtained be related to the measured altitude and thus gain practical interest.

3. **Resistance to vibration.** During the active part of the trajectory, the scientific equipment is subjected to considerable strain (V-2, 6 g; Viking, 7 g; Aerobee, 15 g; WAC Corporal, 60 g). Moreover, the motors generate rather troublesome vibrations (50–130 c/s with an amplitude of 0.5 mm). The scientific equipment and all auxiliary apparatus should therefore be able to stand up to these conditions.

4. **Automation.** All equipment should work automatically, according to a strict schedule. The operation of the automatic equipment should be very accurate and reliable. Special measures should be taken to preserve the data after the rocket's return to the Earth (storage in bulbs, recording on film or tape, etc.), or for transmission of the data to the Earth during the flight.

5. **The "absence" of gravity.** An additional complication when making measurements during the passive part of the trajectory is that all devices designed to make use of the force of gravity (devices involving a pendulum, a falling weight, overflowing mercury, etc.) cannot be used, since the force of gravity acts equally on all parts of the system in free fall so that the various parts of the system cannot move with respect to one another.

The above-mentioned characteristics of rocket investigations, with the possible exception of the fourth point, are not found in investigations carried out with sounding balloons. Because of this, the method of sampling used with rockets differs essentially from that described in the previous chapter.

4. Methods and results of investigations of gaseous composition

The first investigation of the composition of the air by rocket was carried out in 1947. A V-2 rocket launched from the White Sands proving ground (New Mexico, USA) collected samples of air in metal bulbs at an altitude of about 70 km /78/. This experiment was carried out as follows. Steel bulbs, each with a capacity of about 8 liters, were carefully evacuated and sealed. The bulbs ended in tinplated copper tubes, which were opened by a special device at the desired height. When a tube was opened the surrounding air entered the bulb and after a few seconds this tube was pinched and welded to give a hermetic seal. These bulbs were placed in the rocket, with their inlet tubes connected to special chambers under the rocket casing. These chambers communicated with the air surrounding the rocket by means of a number of holes, and were placed so as to intercept a good part of the air flowing counter to the rocket. Assuring the safe return of the air samples to the Earth was a complicated problem. A rocket falling from an altitude of 100 km acquires a tremendous velocity, two or three times that of sound. Moreover, the rocket's tanks still contain unused fuel, which explodes when the rocket hits the ground, causing the rocket to break up into pieces which are scattered over a wide area. Obviously under these conditions it is

impossible to salvage even the steel bulbs containing the air samples. To reduce the rate of fall, the Americans detonated the body of the rocket some distance above the Earth's surface (5–10 km). The explosion was arranged so that the bulbs and the rest of the important equipment were separated from the fuel tanks and fell to the ground independently of them. This explosion naturally caused the various parts of the rocket to lose their streamlining, so that they were strongly retarded in the dense layers of the atmosphere. They thus arrived at the Earth's surface with a speed of about 100 m/sec, and there was a certain chance that the steel bulbs with the samples of air would land undamaged. It was exactly in this way that the first samples of air were obtained from two successful V-2 flights in 1947. The pressure was measured in the recovered bulbs (which had only suffered a few dents), and was found to correspond to the value expected at an altitude of 70 km. This meant that the sampling system was working properly, and that the samples were taken at the desired altitude. The gas was then transferred from the steel bulbs to glass bulbs of about 50 cm^3 volume. Each such bulb contained 2.5 cm^3 of gas (at N. T. P.). Some of these bulbs were sent to Professor Paneth in England for analysis.

In Paneth's laboratory, the samples of air were analyzed for oxygen, argon, helium, neon and nitrogen. Because of the long storage in the bulbs* the composition of the air changed considerably, owing to absorption of oxygen by the walls of the vessels. The main attention was therefore paid to the analysis of the inert gases: the ratios A/N_2+A, Ne/N_2+A and He/N_2+A were determined for the samples and for air from near the Earth's surface. If the atmosphere at the sampling altitude (70 km) was in a state

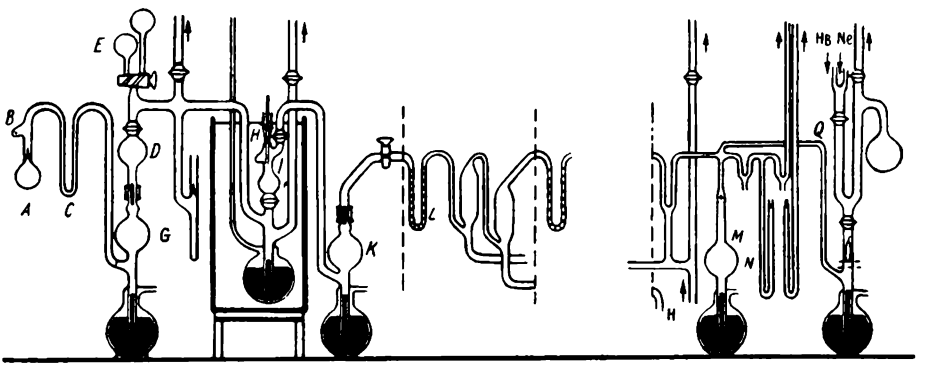


FIGURE 22. Part of the apparatus used by Paneth and Glückauf for the determination of oxygen, water, carbon dioxide, neon and helium

of gravitational separation, the first of these ratios should be less than for air from near the Earth, and the second and third greater. The small size of the gas samples made the work much more difficult, and it was necessary to change the existing analytical apparatus (described in Chapter II). We shall now describe the experimental method used with the new apparatus, which has been used for most of the investigations of the composition of the air at high altitudes carried out outside the USSR.

* In the American investigations, some of the air remained in the bulbs for as much as a year and a half.

Physicochemical method of analysis of high altitude samples. The apparatus of Paneth and Glückauf /79/, used for analyzing high altitude air samples, consists of two parts. The first part, which is used to analyze the oxygen, water, carbon dioxide, neon and helium in the sample, is shown in Figure 22. The sealed bulb A, containing the air sample, is fixed on to the apparatus. After the apparatus has been well evacuated, the bulb A is opened by means of the metal ball B (with the aid of a magnet), and the sample fills the apparatus up to the tap which closes off the bulb D. The U-tube C is cooled in liquid nitrogen; the H_2O and CO_2 of the sample (if present) collect here*. The dry gas is now transferred from bulb A to bulb D with the aid of a Toepler pump. The amount of oxygen present is then measured by absorbing it on a clean, heated copper surface. This is done with the copper coil H (wichh can be heated by an electric current) in the "combustion chamber" I. In order to clean the surface of the coil, a small amount of hydrogen is admitted into the chamber I from the bulb E before the analysis proper, and the spiral is heated in the hydrogen (reduction process); the hydrogen is then carefully pumped out, and the combustion chamber is filled with the air sample. The sample is now compressed by raising the mercury level until it coincides with the end of a pointer fixed to the coil H. The mercury level in the tube J is then carefully read with a cathetometer, and noted. The coil is next heated to a dark red color (~ 500°C) for 1-2 minutes. During this time, the oxygen oxidizes the copper surface, and is completely removed from the sample. After the current has been switched off, the mercury is again adjusted to the pointer level, and the new mercury level in tube J is read as before. The difference between the two pressures of the gas in chamber I gives the amount of oxygen in the sample. Naturally, the chamber must be carefully calibrated first of all. In order to prevent its volume changing with a change in the ambient temperature, the chamber I and the tube J are immersed in a water thermostat whose temperature is kept constant to within 0.1°C. If on repeating the oxygen-absorbing process there is no further change of pressure in chamber I (showing that all the oxygen was absorbed the first time), then the upper tap is opened and the gas is transferred by means of a second Toepler pump K to the second section L of the fractionating system. To determine the oxygen by this method 0.3-0.5 cm^3 of sample (at N. T. P.) are needed. The authors claim that the absolute error of this determination does not exceed 0.3%. The amount of $A + N_2$ remaining (the other inert gases are present in negligible amounts compared to this) is used as the basis to which the amounts of the other gases present are referred, i. e., the ratios $He/N_2 + A$, $Ne/N_2 + A$ and $A/N_2 + A$ are usually determined.

Further analysis is carried out as follows. The fractionating system L, which is now filled with the mixture of nitrogen and inert gases, consists of a series of traps filled with charcoal. It is known that well degassed carbon can absorb large amounts of gases, and that its adsorbing power is

* In general, these samples do not contain appreciable amounts of water or carbon dioxide. If however certain amounts of these substances are present, they may be determined after analyzing for oxygen, neon and helium. For this purpose, the H_2O and CO_2 are frozen out in the trap C, thus removing all of these gases from the whole apparatus. The liquid nitrogen cooling the trap C is then replaced by solid CO_2. The CO_2 in C then evaporates, and its pressure can easily be measured, whence the amount of CO_2 present can be calculated. The solid CO_2 is then removed from trap C, causing the H_2O to evaporate too; the amount of H_2O can then be determined in the same way.

increased many-fold at low temperatures. The carbon traps are therefore cooled in liquid nitrogen. If the gaseous mixture is passed through such a system sufficiently slowly and for long enough, all the gases with the exception of helium are gradually adsorbed by the carbon. The helium passes through and is collected in bulb M, which is connected to a special Pirani gauge N, designed for measuring helium pressures. The total volume connected to this gauge is exactly calibrated. Therefore, if we know the pressure in the gauge we can find the amount of helium in the sample. The whole right-hand part of the apparatus, after the Pirani gauge N, is for the calibration of N for helium and neon (the gauge N has a separate calibration curve for each gas).

After determining the helium in the sample, the helium is removed from the apparatus and the neon can now be determined. Neon, unlike nitrogen and argon, is poorly adsorbed by cold carbon. If therefore the gas sample is passed through the adsorption system at a certain rate, it is possible to ensure that the nitrogen and argon are adsorbed while the neon passes through almost intact. The neon is collected in bulb M, where its concentration is measured in the same way as for helium. This concludes the first stage of the analysis.

The second stage of the analysis, in which the argon in the sample is determined, is carried out in another part of the apparatus, shown in Figure 23. After three independent determinations of helium and neon in the

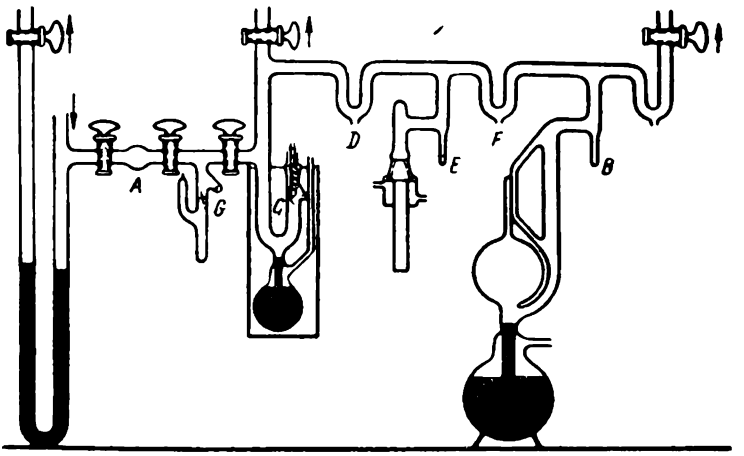


FIGURE 23. Part of the apparatus used by Paneth and Glückauf for determining argon

first part of the apparatus, part of the gas from this sample is absorbed on chilled carbon in the trap G. (Figure 22). After 15 minutes, the trap G is sealed off at the restriction in the connecting tube, and sealed on to the second part of the apparatus, as shown in Figure 23. The apparatus is carefully evacuated. The trap G is then opened by means of a metal ball and the air sample fills the apparatus. The last traces of oxygen are absorbed by a hot copper wire in bulb C, after which the gas is passed through trap D and the carbon trap E. The latter leads to a tubular metal furnace filled with metallic barium (2 gram). The metal tube is connected to the glass apparatus by means of a special seal. In order to adsorb nitrogen

the barium must be heated to 700° C. In order to prevent the grease from melting under these conditions, the taps are continually water-cooled. When the oven has reached the desired temperature, the sample is released from E, and the nitrogen in the sample is adsorbed by the barium for 10–15 minutes. Trap F is now opened, and the remaining gas (argon) is condensed in trap B. This operation takes about an hour, after which the system is evacuated (for exactly two minutes) to remove traces of hydrogen which are unavoidably given off by the barium when the oven is being heated. No argon is lost during the evacuation process, as it is firmly adsorbed on the cold carbon in the trap. Trap F is then closed again, and the coolant removed from trap B so that the argon can evaporate. The argon pressure is measured with the aid of the McLeod gauge. A single operation is almost always sufficient to remove all the nitrogen, leaving pure argon.

Disadvantages of the method. The analytical apparatus is a complicated vacuum system with many taps lubricated with vacuum grease. The weak point of such an apparatus is that it cannot be degassed sufficiently well: in order to degas it thoroughly, one would have to heat the glass, which is quite out of the question under these circumstances. The presence of grease on the taps is also a disadvantage during the use of the apparatus the gas being analyzed comes into contact with the grease, and may be partially absorbed and also contaminated by vapor from the grease. These processes are selective, and may lead to a change in the sample's composition. This effect may be particularly pronounced when investigating small amounts of neon and helium.

Another disadvantage of this apparatus is the large area of glass in contact with the air sample. Absorption on and desorption from this glass may be considerable.

A serious drawback, the limited range of this physicochemical method, is due to the fact that for the reasons mentioned above it is not possible to analyze very small portions of gas in this way. Since the amount of gas in the sample falls off very rapidly with increasing height (see Figure 15), samples taken from altitudes higher than 80 km are likely to contain 1 mm^3 of gas (at N. T. P.), or even less*. Now the minimum amount of gas which can be analyzed in this apparatus can hardly be less than 10 mm^3. This means that the "ceiling" of this physicochemical method is about 80–90 km. We should add that near this ceiling, the accuracy with which the various components of the sample can be determined falls off rapidly. Therefore, reliable results will not be obtained at altitudes higher than 70–80 km.

As we have mentioned above, the first air samples from an altitude of 70 km were obtained on 9 October 1947. These samples were analyzed by Glückauf and Paneth in January 1948. The results of these analyses are shown in Table 21 /79/. The values in the last three columns of this table are expressed in relative units, giving a direct indication of the degree of gravitational separation α of the gases at the sampling altitude:

$$\alpha = \frac{\dfrac{p'_x}{p'_{N_2}}}{\dfrac{p_x}{p_{N_2}}},$$

* Amounts of this order of magnitude will in fact be found at altitudes of about 100 km.

where p'_x and p'_N, are the partial pressures of the gas in question and of nitrogen at the sampling altitude, and p_x and p_N, are the corresponding values at the Earth's surface. If $\alpha = 1$, then mixing is complete; all other values ($\alpha \neq 1$) are an indication of a change of composition with height.

TABLE 21

No. of sample	Height, km	Date of sampling	Date of analysis	α		
				He	Ne	Ar
1 B	70	9 October 1947	4 January 1948	0.953 ± 0.14	0.993 ± 0.08	1.004 ± 0.04
3B	70	27 May 1948	7 Dec. 1948			
15B	54–58	2 June 1949	25 July 1949	1.003 ± 0.03	0.997 ± 0.04	1.010 ± 0.06
16A	50–54	2 June 1949	4 August 1949	0.964 ± 0.03	0.980 ± 0.05	0.996 ± 0.02

On the basis of the results, the authors came to the following conclusions. In the first place, oxygen was absent or practically absent from the samples. However, the authors by no means regarded this absence of oxygen in the samples as indicating the absence of oxygen in the upper atmosphere. They explained this result by suggesting that the oxygen in the bulb was used up in oxidizing the surface of the copper inlet tube at the moment when the latter was being sealed. In the second place, the contents of helium, neon and argon at altitudes of 50–70 km did not indicate any appreciable gravitational separation of the light gases from the heavy ones.

Although the conclusion that there was no separation at these heights was not exactly surprising to experts, this was nevertheless the first definite proof that the atmosphere was still mixed at an altitude of 70 km, and that the level of gravitational separation must lie somewhere higher. This thus removed all doubts remaining from the previous period of investigation, where the results of the analyses carried out with the aid of sounding balloons did not allow definite conclusions to be drawn about the composition of the atmosphere at altitudes of up to 30 km.

Now, "from an altitude of 70 km", we can look back at the difficult earlier course of the investigation. We can now clearly see how naive were the first heroic attempts to conquer the "low" and "medium" altitudes of the atmosphere, when the investigators struggled to gain each kilometer in the hope of finding the level of gravitational separation of the gases. We can also clearly see how these early investigators laid the foundations for the work being carried out at present.

There could be no doubt at all that the level of gravitational separation was situated at some altitude not far from the altitudes already reached; therefore the problem of the composition of the air continued to occupy a position of central importance for investigators of the upper atmosphere. Moreover, as we have already mentioned, the present interest in the composition of the atmosphere is also largely due to the new significance this question has assumed in connection with other problems of the physics of the upper atmosphere.

The first experiments at these altitudes, which we have just described, were followed by others; and the results of these later investigations by no means agreed with the first.

Some air samples taken from altitudes of 40–60 km were analyzed by McQueen in 1949 /80/. He used a mass-spectrometric method of analysis. Since it was not possible to analyze these samples for oxygen, and the concentration of inert gases was much too low for mass-spectrometric work, McQueen analyzed for isotopes of nitrogen, i. e., he determined the ratio of the concentration of molecules with a molecular weight of 28 ($N^{14}N^{14}$) to that of molecules with a molecular weight of 29 ($N^{14}N^{15}$), in the samples in question and in air from near the Earth's surface. The results of his analyses are shown in Table 22. This table shows a completely different

TABLE 22

Height, km	Separation, %
55.4–58.8	3.9 ± 0.4
53.6–57.7	2.7 ± 0.3
49.0–59.8	2.7 ± 0.5
50.4–53.3	0.4 ± 0.3
48.8–47.6	0.8 ± 0.3
41.4–44.9	>0.3

picture of the upper atmosphere from that given by Paneth. Here we see separation of the gaseous constituents of the atmosphere beginning at altitudes as low as 40 km; and moreover we have the important fact that this separation is found between molecular species which hardly differ in their molecular weight.

Such results could not escape the attention of other investigators, and in 1951 Hagelbarger et al. /81/ published a critical paper casting doubt on the results obtained by McQueen. The authors showed in the first place that McQueen had made several errors in determining the altitudes from which the samples were taken, and in the second place they gave the analyses of three samples from those analyzed by McQueen which were also analyzed by Paneth and by scientists in Michigan University. None of these analyses agreed with those of McQueen. These data are summarized in Table 23.

TABLE 23

No. of sample	Height, km	McQueen	Paneth		Michigan University
		separation, %			
		$N^{14}N^{14}/N^{14}N^{15}$	He/N_2+A	Ne/A	He/N_2+A
19B	54.7–58.3	3.9 ± 0.4			
15C	53.6–57.7	2.7 ± 0.3	0.3 ± 0.3	−1.3 ± 0.8	−3
5B	49.0–59.8	2.7 ± 0.5			0
25B	50.4–53.3	0.4 ± 0.3			
20B	45.0–47.8	0.8 ± 0.3			
28B	41.4–44.9	>0.3			−0.3 ± 0.3

In order to justify their doubts, Hagelbarger et al. gave a theoretical calculation which showed that if the separation of the nitrogen isotopes found by McQueen were real, there should be an enormous relative increase in the amounts of helium and neon at the altitudes in question (134 % and 107 % respectively), which could not fail to be detected by the physicochemical method of analysis.

It thus seemed most likely that McQueen's results were due to experimental errors. In fact, McQueen himself had pointed out the large experimental error due to the strong background in the mass spectrometry of the samples.

As far as we know, McQueen was the only person to use land-based magnetic mass spectrometers for analyzing airsamples from high altitudes; and although they were not entirely successful, they did serve to stress once more the importance of the exact determination of the height of gravitational separation.

The first experiments with rockets suffered from a number of defects which were due to the use of sealed bulbs for storing the samples. In order that the further work would not suffer from these defects, it was first of all necessary to examine the sampling technique; this aspect of the experimental determination of the composition of the upper atmosphere is just as important as the actual analysis of the sample once it has been taken. In order to improve the situation, the following two conditions had to be ensured: 1) the air should not be transferred from the steel bulbs to glass ones before sending the samples to the laboratory for analysis, and 2) the device for sealing the bulb after sampling should be modified.

The first of these demands is connected with the fact that helium, one of the elements for which the samples are analyzed, cannot be kept well in glass. In order to get around this very inconvenient fact, Paneth asked for the samples to be sent to him in the steel bulbs in which they were collected. For this, the construction of the steel bulbs had to be somewhat modified: they had to be fitted with a special device to allow the steel bulb to be connected to the glass vacuum system. Special means had also to be devised to allow the gas to be transferred from the bulb to the vacuum system; a thin copper membrane was used which could be pierced by a steel pin.

The need to modify the system for sealing off the air sample was very important, since the opening and closing of the bulb during sampling at high altitudes played a very great role in all experiments*. If we consider the small amount of gas which is collected during the ascents to high altitudes, it will be clear how important it is that the mechanism for opening and closing the bulb should work reliably and cleanly. The slightest trace of contamination, which could be introduced by the improper operation of the sealing mechanism could spoil the whole experiment. It is also important that the air inlet should have a large cross-sectional area, so that on opening, the pressure inside the bulb is rapidly (within a few seconds) equalized with the ambient pressure. This is necessary for two reasons: in the first place, when the flow of air into the bulb during sampling obeys

* Further details about all the demands made on the bulb closure will be given in the next chapter.

Knudsen's equation*, there may be a forced separation of the gases by mass on entering the bulb, which will lead to false conclusions about the presence of gravitational separation in the atmosphere; and in the second place, it is not possible to assign the sample to a given height if the inlet is narrow, since the rocket will have traveled a long way in the time taken to fill the bulb.

It is also important that the composition of the sample should not be altered by the operation of the sealing system. This thus excludes welding the inlet tube by heating.

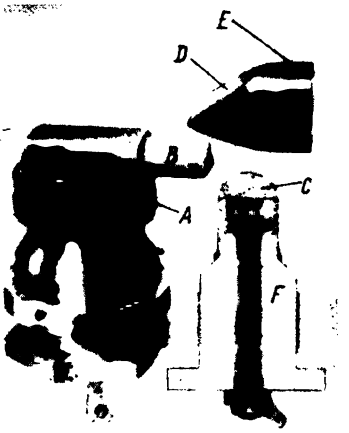
Improved sampling systems are described in the review by Loh et al. /82/. Three methods for opening a sealed metal tube are given in this paper.

In the first method, a triangular knife (Figure 24a) is used to open the inlet tube. The knife B is fixed on to the bellows A, as shown in the figure. The inlet tube E of the bulb is situated opposite the knife and very near to it. The end of the tube is cut off on two sides and covered with copper foil. A small charge C of gunpowder is placed inside A, together with a detonator; wires lead from a battery through the channel F to the detonator. The bellows A are hermetically sealed, so that when the charge C is ignited the pressure in A suddenly increases, the corrugations in A are straightened out, and the knife B rips open the foil D on tube E, so that the surrounding air can enter the bulb. Gas must not escape from the bellows. Such a system for opening the bulb does not always work reliably: in the first place, the hermetical sealing of the bellows is often spoiled by the gunpowder detonation and in the second place the knife sometimes sticks in the tube, blocking the inlet. This made it necessary to give up this opening system in favor of other methods.

In the second method, the end of the inlet tube is cut open with a flat knife actuated by a special motor (Figure 24b). For this purpose, a groove B is cut in the inlet tube D opposite the knife A, making the wall of the tube as thin as possible. The little electric motor C is connected to the knife by a pinion, and when the current is switched on the motor causes the knife to rotate and cut through the groove B in the tube D. This system was used on many flights, but like the previous system it suffers from the disadvantage that the knife tends to block up the hole it makes, so that the air cannot get into the bulb. Moreover, a relatively high-power motor is needed to open the inlet tube, which makes the method uneconomical. It should also be mentioned that when the motor works in vacuo, its windings give off large quantities of gas. Since the motor is placed in the immediate vicinity of the inlet tube, this may lead to considerable contamination of the sample.

The third method has proved to be more effective. The inlet tube of the bulb is opened here by means of the piston A and the yoke D (Figure 24c). At the desired moment, the charge B of gunpowder is detonated, causing the piston A to strike the yoke D with considerable force. The yoke, which is fixed on the end of the tube, can rotate about the axis on which it is held.

* Knudsen's equation for the flow of a highly rarified gas through a tube indicates that the molecules, whose mean free path is considerably greater than the diameter of the tube, do not collide with each other but only with the walls of the tube. As a result of this, there is a marked and characteristic difference between the rate of passage of light and heavy constituents of a gaseous mixture through the tube at a given temperature. This also means that in the nonsteady state, the light, "fast" molecules will enter the bulb in relatively greater quantities than the heavy, "slow" ones.



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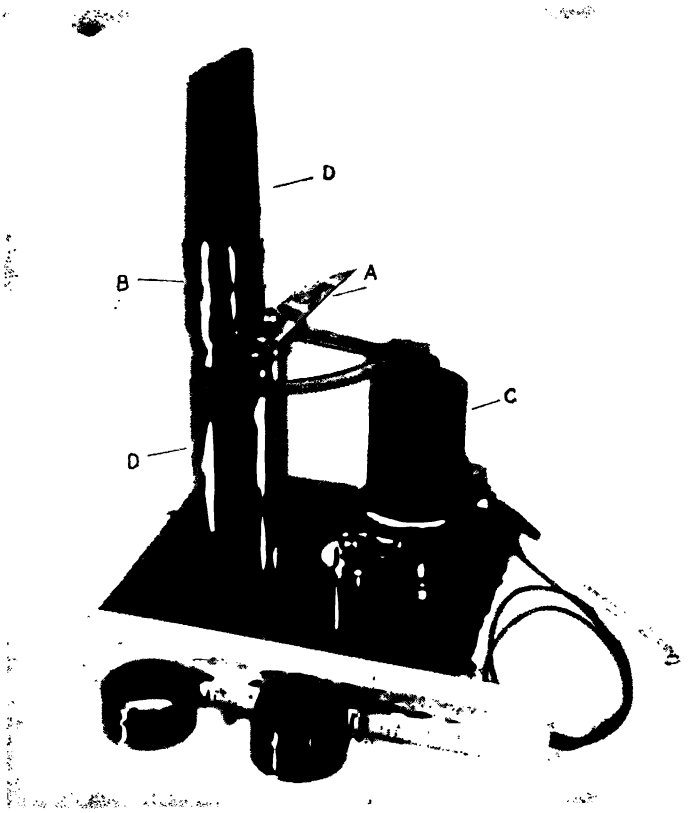

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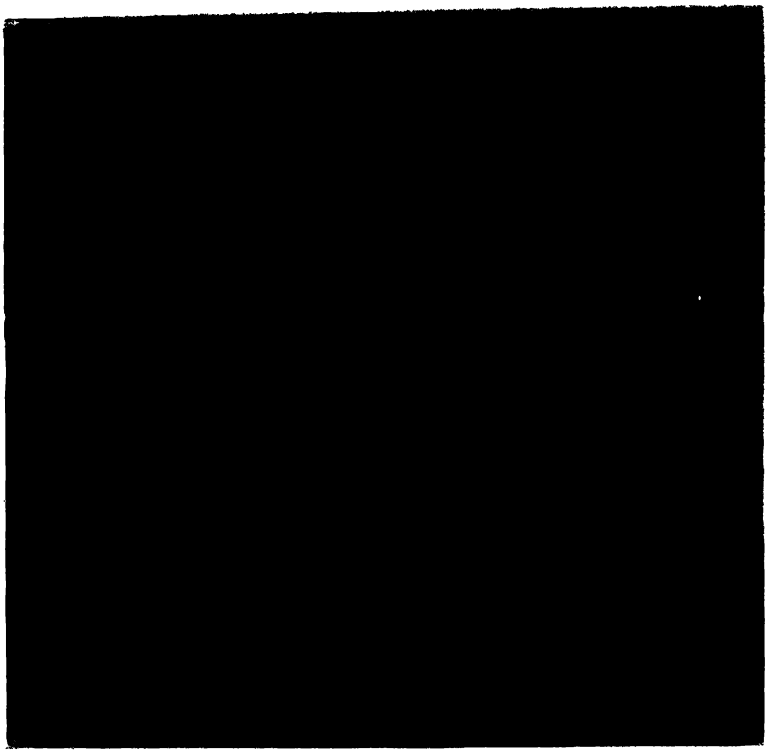

c

FIGURE 24. Systems for opening the inlet tube of the bulb

The powerful blow which it receives causes the yoke to break off the end of the inlet tube E; the end of the tube is removed by a spring. In order to facilitate the opening of the tube, a groove F is made in it, so as to make the wall as thin as possible; the tube is in fact broken open along this groove. The piston A is surrounded by a sleeve to prevent the gas from escaping after the explosion. A special grease is used for lubrication, partly to help in keeping the gas in, and partly to ensure the smooth passage of the piston. Although this is the best method of opening the inlet tube, it still suffers from the same basic disadvantage as the first method: there is a risk that the gas from the explosion will escape and contaminate the sample*.

But opening the tube is only half the battle: the second and yet more exacting task is to close it again.

In the American work under discussion, this was initially done by flattening the tube and welding it tight. However, it very soon became clear that the high temperatures involved in the welding led to changes in the composition of the sample, so it was decided to change to a method of sealing the

* In our opinion, it should be possible to overcome all the disadvantages of the methods described above in a radically simple way: by sealing a thin-walled glass tube on the end of the metal inlet tube. This tube can be broken quite simply and "harmlessly" at the required moment, thus letting air into the bulb. It seems strange that this simple and reliable method was not used in the American experiments.

tube which did not involve welding. Such a system is shown in Figure 25. The inlet tube D of the bulb is placed between two steel jaws E and C. One of these jaws (in the present case C) can move with respect to the other (E), and is connected to the piston B. The motive power for the piston is provided by a charge of explosive A inside it. The ignition of this charge causes the jaw C to move forward at a very high speed; the tube D is thus pinched so forcibly together as to give a vacuum-tight seal (but not every time).

Figure 26 shows a completely assembled bulb for taking air samples. Two disks B and C are slipped over the inlet tube A of the bulb. On the upper disk a device D is mounted for opening the bulb, while the lower disk carries a device E for closing the tube. The piston of the opening device D is mounted in such a way that the gases emitted in large amounts during its operation pass out under the disk; the disk thus acts to a certain extent as a shield, preventing these gases from entering the bulb directly during sampling.

The bulbs were assembled as shown in Figure 26, and were placed in the nose of a rocket (Figure 27). In general, three bulbs B were mounted

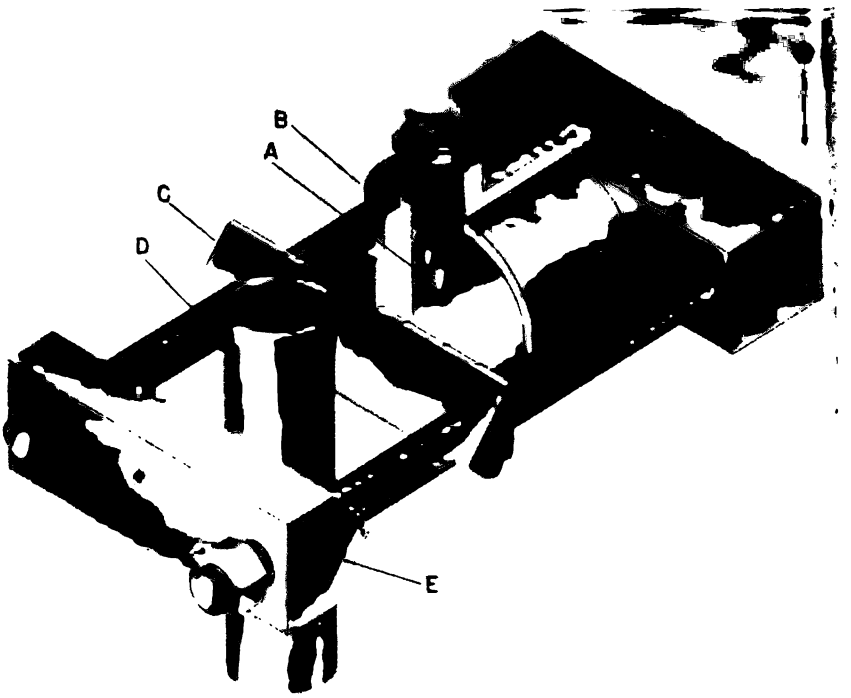

FIGURE 25. System for sealing the opened tube of the bulb

together. The inlet tubes of these bulbs extended as far forward as possible, and ended in the chamber A, which communicated with the surrounding atmosphere via its side vents C.

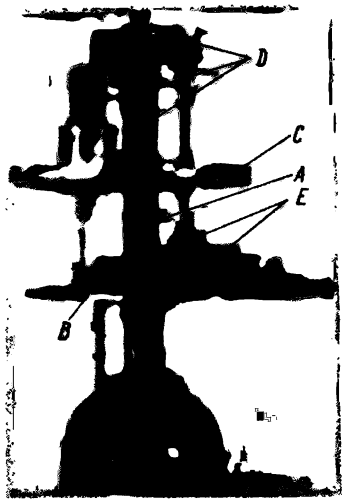

FIGURE 26. External view of the assembled bulb

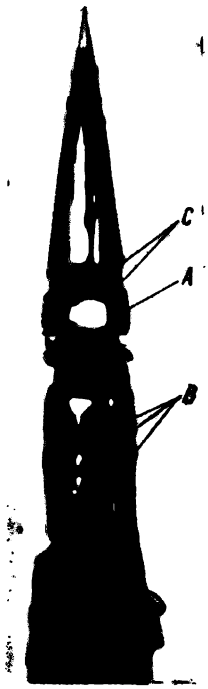

FIGURE 27. The nose of a rocket

At the end of our description of these sampling methods, we should add that the use of "pyrotechnic" methods for this purpose can hardly be said to have been very successful: in the first place, they are not very reliable, and in the second place it is very likely that they cause sample contamination.

Nevertheless, the use of this improved equipment did give results. In 1951, Chackett, Paneth et al. /83, 84/ published new data on investigations of the composition of the air at high altitudes. The samples were taken from altitudes of 64.3-72.0 km. The results are given in Table 24.

Also given in this table for the sake of comparison are the results of earlier investigations in which the samples were kept in glass bulbs before analysis. As may be seen from the table, the duration of storage of the samples in these bulbs varied from two to eight months [sic, see 19D].

As we have already mentioned, in this case no gravitational separation of gases could be found at the altitudes in question. However, the authors of these papers were inclined to think that the failure to discover separation of the gases was due to the faulty experimental method, namely the use of glass bulbs for prolonged storage of the samples (helium dissolves in glass and diffuses through it).

The other group of samples was stored in steel bulbs. The results of the analysis of these samples indicated gravitational separation in the atmosphere, starting at an altitude of 60 km; and according to the authors this could not be due merely to experimental error. It is true that samples B-8 and B-9 were not obtained quite according to plan (which naturally reduces the value of the deductions made from these results): during the opening of the inlet tube of bulb B-8, the knife stuck in the opening so that

TABLE 24

No. of sample		Height, km	Date of ascent	Date of analysis	α*			
					O_2	He	Ne	A
B-13	Steel bulbs	55.6–58.2	26 Nov. 1951	23 Nov. 1951	0.50	0.998	1.005	1.001
B-15		58.2–60.3	26 Nov. 1951	18 Dec. 1951	0.01	1.035	1.008	0.996
B-6		64.3–67.0	19 Dec. 1950	12 June 1951	0.07	1.44	1.08	0.93
B-8		67.0–69.6	19 Dec. 1950	25 June 1951	0.25	2.02	1.18	0.89
B-9		69.6–71.8	19 Dec. 1950	9 May 1951	0.03	2.41**	1.20**	0.85**
16A	Glass bulbs	49.6–53.6	2 July 1949	4 Aug. 1949	0.61	0.96	0.98	1.00
25D		50.4–53.3	6 Dec. 1949	17 April 1951	0.60	0.98	1.00	1.00
15B		53.6–57.7	2 June 1949	25 July 1949	0.12	1.00	1.00	1.01
19D		54.7–58.3	21 July 1949	6 March 1951	0.00	1.01	1.45	1.01
3B		55.4–65.5	27 May 1948	1 Dec. 1948	0.02	0.98	0.99	0.99
1B		61.1–72.0	9 Oct. 1947	4 Dec. 1948	0.02	0.93	1.00	1.01

* See p. 68.

** Results corrected for the presence of 400% of air from the Earth's surface in the sample [sic].

the air could not flow in properly. The pressure in this bulb was thus less than expected. The pressure in sample B-9, on the other hand, was five times more than expected. This means that bulb B-9 was not hermetically sealed, so that air continued to flow into the bulb until it was found and sealed with picene. In fact, bulb B-9 was still found to have a leak when it arrived in the laboratory. Assuming that the sample contains 4/5 of air from near the Earth's surface, we can calculate the concentrations of the gases in question in the remaining fifth of the sample. Table 24 gives the figures obtained from sample B-9 corrected for "impurities" in this way. If this estimate is to be relied upon, then the results from the last three samples of Table 24 show a fairly regular increase in the gravitational separation of gases with height. The concentration of A, Ne and He (referred to the concentration near the Earth) is plotted as a function of height in Figure 28 in accordance with these results. As can be clearly seen from this graph the concentration of helium increases rather suddenly at a height of about 60 km, while the concentration of neon also increases, though not so rapidly. The concentration of argon falls slightly with increasing height. The picture agrees qualitatively with that expected for the gravitational separation of gases in the atmosphere. It is difficult to compare the results quantitatively with theory, since at the altitudes in question turbulence and wind mixing processes occur.

The results of these investigations force us to look for an explanation of the discrepancy between the theoretical prediction of gravitational separation at altitudes exceeding 100 km and the results of direct experiments indicating

separation of gases at an altitude of 70 km. Since the observed separation is so slight as to be no more than a hint of a separation, many investigators were of the opinion that this discrepancy between theory and experiment was the result of errors in the latter.

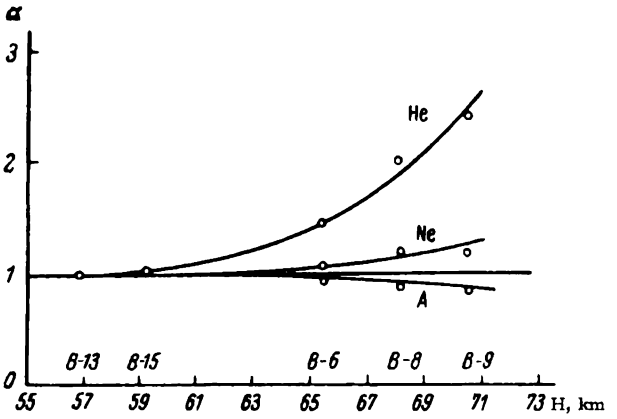

FIGURE 28. Gravitational separation of gases as a function of height

Further confirmation was needed of the fact of separation at these heights, so surprisingly low according to the theoretical calculations. This confirmation was provided in 1952, when three more samples (C-1, C-3 and C-5) were obtained from altitudes of 66–90 km with the aid of a V-2 rocket /85/; analysis of these samples confirmed the earlier findings that the relative content of helium and neon increased with height, while that of argon decreased.

Conclusion

On the basis of the careful investigations described above, it could confidently be stated that a boundary existed somewhere below an altitude of 100 km, which defined a level of gravitational separation at least for the atmospheric inert gases.

TABLE 25

No. of sample	Height, km	α*			
		He	Ne	A	O_2, %
B-13	55.6–58.2	0.998	1.005	1.001	10.5
B-15	58.2–60.3	1.035	1.008	0.996	0.2
C-11-B	57.0–64.3	1.133	1.040	0.962	15.3
B-6	64.3–67.0	1.44	1.08	0.929	1.8
C-5	64.3–71.0	1.57	1.23	0.90	0
B-8	67.0–69.6	2.02	1.18	0.89	6.8
B-9	69.6–71.8	2.41	1.20	0.85	0.7
C-1	84.4–89.0	2.95	1.39	0.82	0
C-3	89.0–93.2	–	–	0.82	0

* See p. 68.

All the recent data obtained outside the USSR on the composition of the upper atmosphere are summarized in Table 25. Here, as before, the figures in the table give the relative increase or decrease in the concentrations of the various gases, referred to the corresponding values at the Earth's surface.

The data shown in this table are all that have been obtained outside the USSR on the composition of the atmosphere at high altitudes, using the method of taking samples in bulbs. A large series of similar measurements have been carried out in the Soviet Union, making use of methods which differed considerably from those described above. All this work will be described in detail in the next chapter.

Chapter IV

SOVIET INVESTIGATIONS OF THE COMPOSITION OF THE UPPER ATMOSPHERE USING ROCKETS (sampling method)*

Introduction

Rocket investigations on the chemical composition of the atmosphere began in the Soviet Union in 1949, i. e., at about the same time as similar work in other countries**.

The Soviet work differed from that done in other countries in the methods of obtaining the atmospheric samples and of their analysis (the sampling was done a considerable distance from the rocket).

The powerful Soviet rockets, capable of lifting large loads, were fitted with special mortars in which the automatic containers for the measuring equipment (including the sampling bulbs) were placed. At a given height, specified in the rocket's flight program, the containers were shot out of the mortars and described independent trajectories in the Earth's gravitational field. The mortars were placed at an angle to the axis of the rocket, so that the containers were projected laterally from the rocket, thus outstripping it and avoiding the danger zone in which the composition of the atmospheric gases can be very considerably falsified by the "stray" gases surrounding the rocket. The container was ejected from the mortar some time before the rocket reached the sampling altitude. This was done so that the container could get as far away as possible from the rocket, and could be thoroughly "ventilated", so as to remove traces of contaminating gases which are always present in small amounts in the container. After the equipment in the container had performed its task and the container had started to fall, a parachute opened, bringing all the fragile glass equipment gently back to Earth.

Unlike the American and English scientists, who used a physicochemichal analysis method for their air samples, the Soviet scientists used a spectroscopic analysis method. This analysis method allowed quantities of gas amounting to a tenth or even a hundredth of a cubic millimeter (at N. T. P.) to be analyzed quantitatively for their main components (oxygen, nitrogen, argon). In this way investigations on the composition of the atmosphere chould be carried out with satisfactory accuracy (5-8 %) up to altitudes of about 110 km.

* This chapter is largely based on our previous publication /86/.

** American work on the taking of samples of the atmosphere began at the end of 1947 (the first samples being analyzed at the beginning of 1948), but the methods and results of the work done before 1949 have not yet been published.

A characteristic of rocket investigations on the composition of the atmosphere is the particularly clear division of each experiment into three parts: the sampling, the storage of the sample, and its analysis. Each of these parts has its own significance, and we shall discuss them separately in the next three sections.

1. Sampling

We used glass bulbs fitted with special taps for taking our air samples. These bulbs were placed in containers, which were carried to the desired height by rocket.

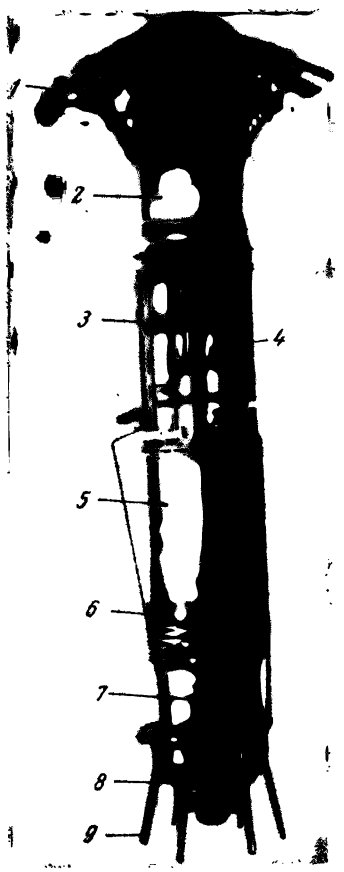

FIGURE 29. The automatic container

1–retarding vane system; 2–parachute compartment; 3–open compartment; 4–glass bulbs; 5–instrument compartment; 6–window supplying light to cameras; 7–power-supply compartment; 8–buffer cone; 9–steel legs to help buffer container's fall on the Earth.

The container. The container, which is shown in Figure 29, consists of a metal cylinder about 3 m long and 40 cm in diameter. It is divided into a number of separate compartments: the parachute compartment 2 at the top, then the open, easily ventilated compartment 3 containing the measuring equipment, followed by the instrument compartment 5, and finally the power-supply compartment 7. A system of retarding vanes is mounted on the cover of the parachute compartment cover. These slow the container down and orient it while the parachute is not in action. At the other end of the container there are a thin corrugated metal cone and steel legs which act as a buffer system, softening the container's arrival back onto the Earth at the end of its parachute drop.

Two basic conditions were imposed on the construction of the container: the realization of the planned program of investigations, and the absence of any gaseous contamination. The latter largely depends on the cleanness of the surfaces, the ease of washing these surfaces, and the absence of pockets in which air from the Earth can be lifted to high altitudes, where it slowly emerges and contaminates the surrounding space. The auxiliary compartments 2, 5 and 7 are therefore hermetically sealed, while compartment 3 on the other hand is made as open as possible to ensure free access of the surrounding air to the measuring equipment.

The absence of contamination is naturally of extreme importance when taking air samples. The parachute packed in the parachute compartment, which acts as an enormous reservoir of air from near the Earth, gives rise to large contamination difficulties. Much of the tightly packed material does not have a chance to give off the gas during the rocket's ascent, therefore a special sealing system is used for the parachute compartment. The whole parachute compartment is enclosed in a metallic safety cover standing on a supporting plate, so that the whole "danger zone" is hermetically sealed. The safety cover is not discarded until just before the parachute is opened, after the whole program of scientific measurements in the container has been completed (including the sampling).

For the proper functioning of all the automatic equipment and the power-supply units in compartments 5 and 7, it is necessary that atmospheric pressure should be maintained in these compartments. Since the surfaces of these compartments are smooth, they can be easily and thoroughly washed and degreased before the flight.

The open compartment in which the sampling bulbs are placed, is shown separately in Figure 30. To ensure a sufficient vacuum in this compartment the only materials used in it are metal, glass and porcelain, and a minimum amount of vacuum rubber used as packing where the glass bulbs are fixed on to an internal metal cross-bar.

The necessary voltages and the control signals from the programming unit are led from compartments 5 and 7 to the devices for opening and closing the bulbs via bare copper bars supported on porcelain insulators.

Recently, a new type of open compartment was used, which allowed the bulbs to project somewhat out of the body of the container. Such a compartment is shown in Figure 31. This modification was made because the analytical results indicated that at the high altitudes under investigation the samples were contaminated by gases evolved from those surfaces in the container which were "visible" from the inlet of the bulb. (At altitudes of about 110–115 km, the mean free path of the molecules is so great that

molecules from surfaces which are "visible" from the inlet of the bulb can pass unchecked into the bulb, thus causing errors in the composition of the

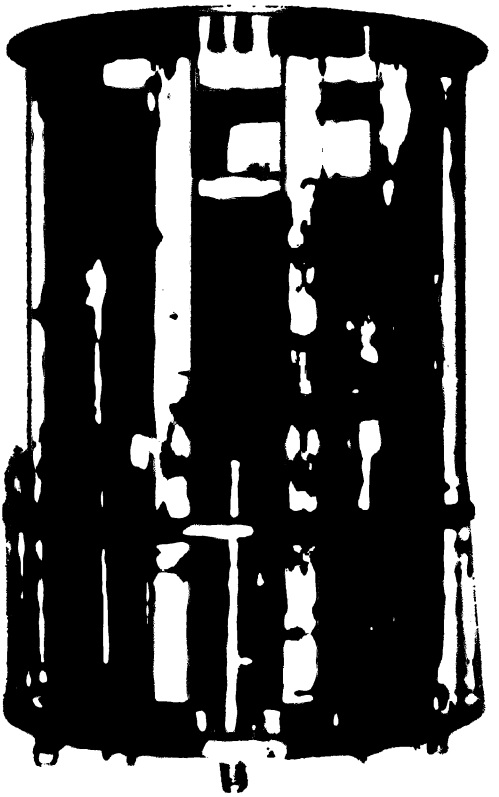

FIGURE 30. The open compartment of the container with the bulbs for taking samples at altitudes below 100 km

atmospheric air.) It was therefore necessary to give the bulb such an orientation that the sample would be substantially free from contamination*.

Before the flight, the loaded container is carefully washed with alcohol and rubbed dry; it is then brought to the rocket at the launching site in a special covering. It is placed in the mortar in such a way that when the covering is removed it is handled as little as possible. The aim of these precautions is to keep the contamination of the surrounding medium, whose parameters have to be measured by the container, to a minimum.

The bulbs. Unlike the Americans, who used steel bulbs for taking air samples, we used glass bulbs. There is a good reason for this. Since we

* This precaution is not necessary at lower altitudes (less than 100 km), because the mean free path of the molecules is still small there, and the concentration of surrounding gas is sufficient to make the desorption of gases from (well prepared) surfaces negligible.

were analyzing the samples for oxygen, we could not use metal containers for storing these samples: because of its great chemical activity, oxygen

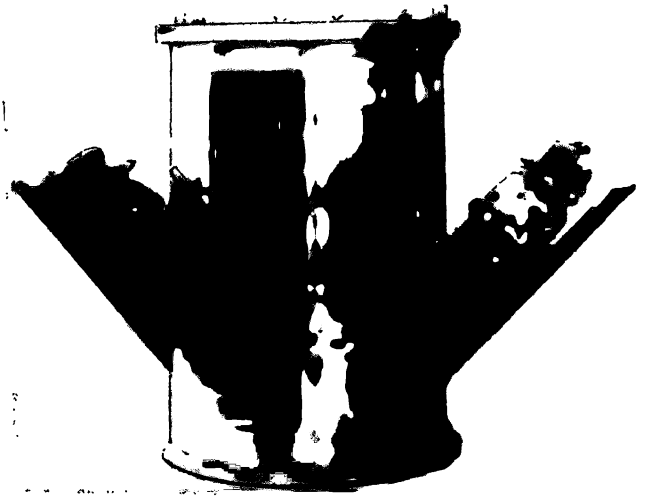

FIGURE 31. Compartment of the container with projecting bulbs for taking samples at altitudes above 100 km. Before and after sampling, the flaps are closed

normally oxidizes metallic surfaces and is thus lost for analysis*. The walls of a glass bulb are undoubtedly better in this respect. Unfortunately, it is a very difficult matter to recover glass bulbs intact. However, we managed to solve this problem and we were able to use this method to collect quite large samples at altitudes of about 100 km.

In our published work /86/ we used thin-walled glass bulbs with a volume of about three liters. The sample collected in such a bulb at altitudes of 80–95 km gave 3–4 mm^3 of air (at N. T. P.) in the laboratory. Since spectroscopic analysis can be carried out with considerably smaller amounts, we also used smaller bulbs with a volume of 400 cm^3. A sketch of one of these small bulbs is shown in Figure 32. The smaller bulbs, which are less fragile, are to be preferred as regards recovery. Both types of bulb are shown in Figure 33.

The preparation of the glass bulb for the flight consists of two stages: a preliminary one, and a final one just before the flight.

The preliminary treatment consists in subjecting the bulb with its closing device (which we shall be describing shortly) to a special thermovacuum treatment to remove moisture and occluded gases. The bulb is washed with alcohol and evacuated for 8–10 hours to a pressure of about 10^{-6} mm Hg, the glass being simultaneously heated to 300–400°C.

The pre-flight treatment is necessary because the bulb is not used immediately after the preliminary treatment, but may be stored for several months before the flight. During this time, the inside of the bulb may evolve

* As we have already mentioned, this explains the absence of oxygen in the steel bulbs used by the American investigators.

a certain amount of stray gases. The bulb is therefore evacuated again just before the flight. For this purpose, the bulb is fitted with an extra

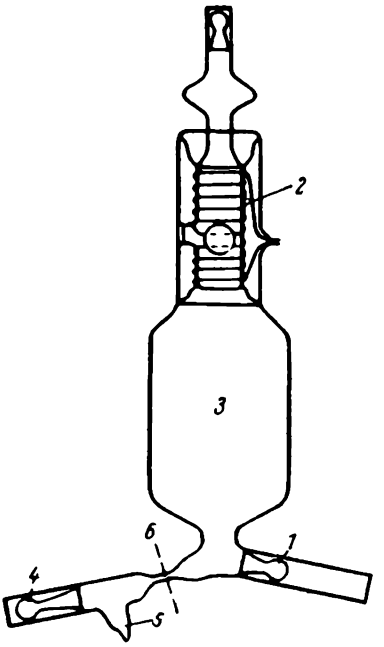

FIGURE 32. The small glass sampling bulb

1–side arm for connecting bulb to vacuum apparatus for analysis; 2–tap with heating coil; 3–bulb; 4–spare-side arm for pre-flight evacuation; 5–place where bulb is sealed after initial evacuation; 6–restriction for sealing bulb after pre-flight evacuation.

side arm by which it can be sealed to the vacuum line and then sealed off without any air entering. This operation is carried out the day before the

FIGURE 33. Large and small glass sampling bulbs

These bulbs are provided with automatic taps lubricated with ceresin.

flight with the mobile high-vacuum equipment shown in Figure 34*. The bulb is not heated this time.

FIGURE 34. Portable high-vacuum equipment

This method of preparing the bulbs has the advantage that it allows the vacuum-tightness of the closing device to be checked: if the pressure in the bulb is found to have increased before the pre-flight evacuation (to 10^{-4} mm Hg or more), the bulb in question is rejected.

The closing device. The most important part of the bulb is the closing device. If we use glass bulbs, we have to use glass closing devices too, since the use of some kind of metal plug would annul all the above-mentioned advantages of using glass.

Since the amount of gas collected in the bulb only amounts to about 0.01–1 mm^3 at N. T. P., the closing device must meet the following stringent demands:

1) before and after sampling the closing device should give a perfect seal;

2) the processes involved in the operation of the closing device should not produce stray gases in amounts capable of appreciably contaminating the sample. If the closing device is greased, the grease should not enter into reaction with the gases of the sample;

3) the inlet of the closing device should be short and wide. If this is not so, in those regions of the atmosphere where the mean free path of the molecules is larger than the dimensions of the inlet (the Knudsen range), there may be a forced separation of the gases according to their molecular weights: the light gases will enter the bulb more quickly than the heavy ones**;

4) the closing device must be able to work properly a long time after it is "loaded". This time, like the time spent in storage before the flight,

* Equipment designed by A. A. Baikov.

** See note on p. 72.

may amount to months. It would be very desirable to have a closing device which would allow the bulb to be opened and closed more than once, so that its operation can be repeatedly checked in the laboratory;

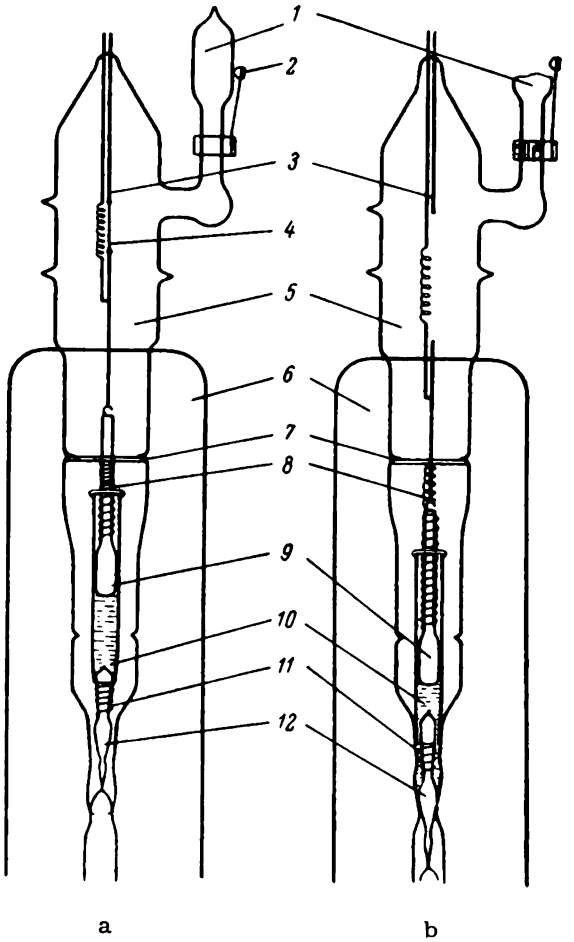

FIGURE 35. Sketch of mercury closing device, a. before and b. after sampling:

1–end of inlet tube; 2–hammer for breaking end of inlet tube; 3–electrode which also supports the inner part of the closing device; 4–part of the electrode which is melted by the current when the bulb is closed; 5–external part of closing device; 6–neck of bulb; 7–retaining disk; 8–spring; 9–ground-glass stopper; 10–mercury filled pump; 11–spring; 12–ground-glass stopper for outlet valve.

5) the closing device should work automatically, should be as simple as possible and compact, and should not consume much power from the supply batteries.

It was by no means an easy matter to make a closing device which met all these demands. In our attempts to solve this problem we tried out a large number of different types of closing devices. Here are some of them:

1) normal vacuum tap with vacuum grease;

2) melting the inlet tube of the bulb by means of a heating coil, and then flattening the heated part of the tube;

3) melting with a heater coil the inlet tube of the bulb, which contains a dry ground-glass stopper, thus sealing the ground surfaces together;

4) a ground-glass stopper, sealed in by the action of silver chloride;

5) closing device with optical contact;

6) vacuum tap lubricated with picene, the picene being melted during the operation of the tap;

7) mercury closing device;

8) vacuum tap lubricated with ceresin (melted);

9) closing device with flat ground-glass surfaces, lubricated with ceresin (melted).

By no means all of these possibilities proved suitable for practical use. For example, it was very soon found that a vacuum tap with normal vacuum grease was unsuitable for this purpose. In the first place, the grease entered into chemical reaction with the oxygen in the sample; in the second place, on prolonged storage the grease dried out, and the tap became difficult to turn; moreover, the tap then no longer gave a good seal; and in the third place the drying of the grease meant that the lighter fractions evaporated, contaminating the sample.

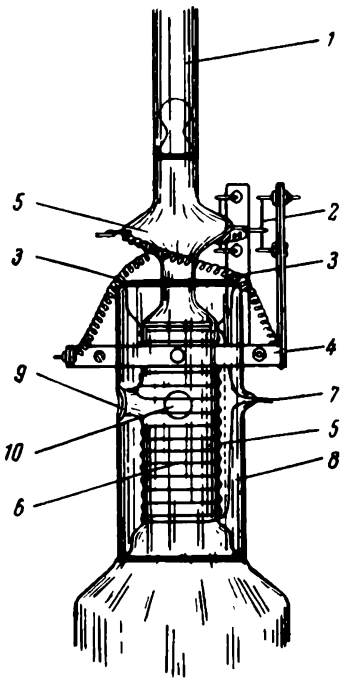

FIGURE 36. Vacuum tap with ceresin

1–tube for sealing bulb with sample on to vacuum apparatus; 2–stop; 3–springs; 4–metal collar; 5–supporting bulge; 6–heating coil; 7–leads of heating coil; 8–outer jacket; 9–inlet to bulb; 10–inlet in stopper of tap (the tap is shown in the closed position).

All closing devices involving the melting of the glass, which worked perfectly well when sampling at low altitudes (up to 30 km), proved completely unsuitable when sampling at altitudes of about 100 km. As is known /87/, when glass is melted, large amounts of gases such as CO, O_2 and CO_2 are inevitably evolved. When the surrounding medium is relatively dense (at low altitudes), the melting of a narrow capillary does not give off enough gas to contaminate the sample appreciably. A different picture is found when sampling at high altitudes: the atmospheric pressure is low (10^{-3} – 10^{-2} mm Hg) and the inlet tube must be wide (see above), which leads to considerable contamination of the sample.

Somewhat the same trouble is found with picene and silver chloride. When these substances are melted, large amounts of stray gases are evolved. Moreover, silver chloride required rather a high temperature and did not always give a good enough vacuum-tight seal.

Closing devices involving the contact of two optically flat surfaces could not be designed for our present purpose: the auxiliary equipment involved was too heavy and complicated, and could not be relied upon to work properly.

Only three of the closing devices we tried proved suitable for practical use: the mercury closing device, the vacuum tap lubricated with ceresin and the sealing device with flat ground-glass surfaces, also lubricated with ceresin. We shall pause for a brief description of these closing devices which we used in our work /86/.

The mercury closing device sketched in Figure 35 involves the use of dry ground-glass stoppers, mercury and springs. The operating principle is briefly as follows: after the evacuated bulb has been opened and the sample taken, the inlet tube of the bulb is closed by means of two ground-glass stoppers the space between which is filled with mercury. This use of a mercury "stopper" combined with ground-glass seals gives an excellent vacuum-tight seal. This closing device has however two serious disadvantages: it is bulky and fragile. It was therefore later replaced by the simpler and more convenient tap with ceresin.

This closing device was a normal vacuum tap, very carefully ground to give a good seal, with an inlet area of about 1 cm^2. It was lubricated with ceresin (mineral wax) — a mixture of high-polymer paraffins ($C_n H_{2n+2}$); it is a solid at room temperature, and melts between 60 and 100°C, depending on the conditions of its distillation. Our experiments showed that neither solid nor molten ceresin, which had been distilled in a vacuum, gave off stray gases in amounts which could affect the analytical results. Moreover, thanks to its chemical inertness, it does not react with any of the main components of the samples (N_2, O_2, A). The mechanical properties of ceresin are also particularly suitable: in the solid state it has great mechanical strength, and in the liquid state a very low coefficient of viscosity. The stopper of the tap thus turns very easily when the ceresin is molten, and is fixed tight by merely cooling the ceresin. If the stopper is well ground, cooling the ceresin gives a faultless vacuum-tight seal.

The construction of the tap itself is relatively simple (Figure 36). The tap is turned by two spiral springs 3. A heating coil 6 is fixed on to the supporting bulge of the tap 5. This coil is separated by a glass jacket 8 from the surrounding space. The closing device is also provided with a stop 2 which holds the tap in the necessary position and then releases it. This stop consists of a short wire, which prevents the tap from turning; it may be melted by an electric current at the appropriate moment, thus allowing the springs 3 to turn the tap. Before the start, the tap is in the "off" position, i. e., the inlet is closed and sealed tight by the cold ceresin, and the springs are under tension. When the sample has to be taken, the ceresin is melted by the heating coil, thus freeing the tap, which makes a quarter turn under the influence of the springs, and is kept in this position (with the inlet open) for 10 seconds by the stop. During this time, gas flows into the evacuated bulb until the pressure inside is equal to that of the surrounding atmosphere. The stop is then melted by the passage of current, and the tap turns further, closing the inlet again. The heating coil is then turned off, and the ceresin solidifies, giving a good vacuum-tight seal.

The switching on and off of the heating coil and the melting of the stop are brought about by a control unit at a closely defined moment of time. Thanks to this, the height of sampling is always accurately known. Moreover, at the moments of opening and closing the bulb a signal lamp lights up in the equipment compartment, which is photographed together with other equipment on film. The sampling height can then also be calculated from this photographic record.

The closing device with flat ground surfaces was the most satisfactory, allowing a large inlet cross-section and a short neck on the bulb to be used. This closing device is shown in Figure 37. It works as follows. A recessed flange is made on top of the neck of the glass sampling bulb, and a Nichrome heating coil is wound inside this flange, the leads being sealed into the glass.

FIGURE 37. Closing device with flat ground surfaces, in the open (a) and closed (b) positions

1–opening spring; 2–rotation mechanism; 3–top half of sealing device; 4–closing spring; 5–stops for 3; 6–flange on neck of bulb; 7–heating coil; 8–lug for electrical supply leads; 9–tube for sealing bulb on to vacuum apparatus; 10–sampling bulb.

This heating coil is used to warm the ceresin. The top surface of the flange is ground flat, with an accuracy of 1–2 microns. The top half of the closing device, shown in Figure 37, is also carefully ground flat. The two surfaces ground in this way and lubricated with a thin layer of ceresin give a good vacuum-tight seal. Unlike the normal vacuum tap, this closing device with flat surfaces still maintains the vacuum when the ceresin is melted, even when the pressure difference across the closed seal is as much as one atmosphere.

The mechanism for opening and closing the inlet of the bulb (diameter 3 cm)*, suggested by A. A. Bailov, also makes use of a system of spiral springs. The bulb is opened automatically when the ceresin is melted, the extended springs pulling the top half of the closing device to one side as

* One would have to use an enormous vacuum tap of the normal type to give such a large inlet: the diameter of the stopper of the tap near the inlet would have to be about 10 cm.

they contract. After the bulb has been open for the necessary time and the stop melted, the top half is pulled back to its original position, this time by another spring. In order to prevent the closing device opening accidentally after sampling and before the ceresin has solidified, the top half of the closing device is fixed by a special attachment which prevents lateral (sliding) motion*. The necessary voltages and control pulses are supplied in the usual way by the programming unit in the instrument compartment of the container.

2. Storing the samples

Some time passes between the taking of the sample and its analysis, therefore careful attention must be paid to the method of storing the minute amounts of gas obtained so that their composition does not change.

At altitudes of about 100 km, where the samples were taken, the mean free path of the molecules is a few centimeters. The gas molecules in the bulb therefore undergo frequent collisions with the walls. Under these circumstances, there will be considerable adsorption of gas on the walls, and the composition of the gas may be expected to change appreciably. Moreover, these conditions are favorable for the desorption of stray gases from the walls, which may also lead to a departure from the initial composition of the sample.

In order to reduce the above-mentioned undesirable effects to a minimum, the length of time between sampling and analysis should be reduced as much as possible. In the experiments described here, this period was reduced to 2–5 days, but even this was not enough. Moreover, the question of the prolonged storage of gas samples is still of extreme interest, because of the necessity of keeping the samples in the laboratory for duplicate measurements, and of storing mixtures of known composition used for calibration.

All the above-mentioned considerations led us to develop the "capillary method" for the prolonged storage of small amounts of gaseous mixtures.

The capillary method of storing small amounts of gas

As is known, sorption effects depend on the surface available to the gas. If we want to stop changes in the composition of the gas sample, we must reduce as much as possible the area of the surface with which it is in contact. This can be done by transferring the sample as soon as it is received from its bulb, where the pressure is of the order of a thousandth of a millimeter of mercury, to a narrow capillary. The sample is then compressed to atmospheric pressure. This transfer is done in the vacuum apparatus used for the analysis, with the aid of mercury (see section 5). After the gas has been compressed in the capillary, it is kept in by a droplet of mercury, which forms a hermetic seal. Figure 38 shows a glass capillary cut from the vacuum apparatus, with a small portion of gas "sealed" into it. Samples may be kept in such capillaries for a long time. Our experiments showed that samples (of normal air) did not change their composition when stored in this way for a period of 2–3 years. With samples containing helium, however, the helium did diffuse through the

* This motion could be caused by the pressure forces arising after sampling when the container is falling at high speed through the relatively dense layers of the atmosphere.

glass (quartz) and slowly disappear from the capillary*. When the volume in which the gas is contained is reduced, the ratio of its surface area to its volume will in general increase; it would thus seem as if the storage and analysis of the gas in a small volume would precisely enhance the surface effects (see for example /88/). However, an investigator who has to

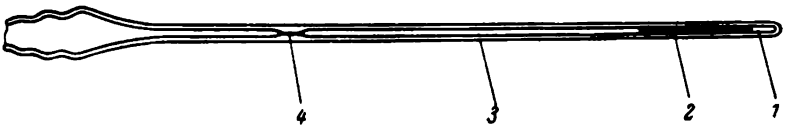

FIGURE 38. A capillary with a "sealed-in" sample of gas

1–gas sample, compressed to atmospheric pressure; 2–mercury "plug"; 3–capillary; 4–constriction for retaining mercury.

perform a microanalysis on a limited amount of a gaseous mixture would be wrong in making this assumption. When a given portion of gas is compressed, the amount of gas remains the same, no matter how small the volume in which it is contained, while the area of the surface containing the gas will naturally decrease as the volume is decreased. For a given portion of gas in the analytical cell, and also for the storage of this portion of gas, what matters is not the ratio of the volume of the vessel containing the gas to its surface area, but the absolute value of the latter.

The transfer of the gas sample from the bulb to a narrow capillary can reduce the area of glass available for sorption effects by many orders of magnitude. For example, when gas at a pressure of 10^{-3} mm Hg is transferred from a bulb with a volume of 3 liters (surface area about 2×10^5 mm^2) to a capillary of diameter 0.3 mm, the pressure being increased to atmospheric, it will occupy a volume of about 0.3 mm^3 (surface area about 3 mm^3); the "harmful" area has thus been decreased by more than fifty thousand times. These conditions are certainly very favorable for storing samples.

When the capillary method is used, the fact that the gas is under a relatively high pressure is also very important for "preserving" the gas, since it keeps the mean free path of the gas molecules very low. At atmospheric pressure, the mean free path does not exceed a few millionths of a centimeter ($\sim 5 \cdot 10^{-6}$ cm), therefore most molecules collide with each other, and not with the walls as they did previously. Moreover, the walls themselves are no longer so dangerous for the sample, since they are covered with a stable layer of absorbed gas, which hinders any further sorption effects /91, 87/.

The storage of the air samples in capillaries also had other important advantages for us. One of these is that the storage capillary also acts as an excellent manometer, allowing the pressure of the sample in the bulb to be very accurately determined. Knowing the diameter of the capillary and measuring the length of the column of gas under the mercury seal with the aid of a lens, one can easily calculate the volume of the gas in the capillary under the given atmospheric pressure. Knowing the volume of the bulb

* If the capillary contains pure helium, the reduction in the length of the column of gas gives a simple and accurate measure of the diffusion of the helium through various sorts of glass and quartz.

from which the gas was transferred to the capillary, one may hence calculate the original pressure of the gas in this bulb. Thus, a necessary operation (the measurement of the original pressure in the bulb containing the high-level sample of air) is reduced to the simple measurement of the length of the gas column in the capillary. This measurement can be made to within a relative error of 2–3%, in other words the capillary method allows us to determine the pressure in the bulb with an accuracy of 2–3%*. Such an accuracy may be considered high, since pressure gauges at present used in vacuum techniques for measuring pressures of the order of 10^{-3} mm Hg have, at the very best, an accuracy of 20–30%.

The advantages of this method of measuring the pressure are particularly clear when one is dealing with very small gas samples. In this case, any other method will lead either to a change in the sample's composition owing to impurities (ionization gauge, thermal and other types of pressure gauges) or to a considerable loss of gas, which gets left behind in the manometer (mercury manometer, etc.). The capillary manometer, being an "absolute manometer", is free of these disadvantages.

Another great advantage of the capillary method is that, once the gas is in the capillary, it cannot flow in any direction, so that it cannot be contaminated or lost in the rest of the vacuum apparatus. Anticipating ourselves somewhat, we shall also mention that the spectral analysis can be carried out directly in the capillary in which the gas is stored. For this purpose, the "sealed-in" gas must be given a suitable pressure, about 5–10 mm Hg. This pressure can be produced by withdrawing the mercury plug the appropriate distance with the aid of an ordinary backing pump, a restriction being placed in the capillary to stop the mercury from going too far. The pressure in the capillary cell can simply be checked by measuring the length of the gas column again. After the analysis is completed, air is simply admitted into the free end of the capillary so that the mercury plug returns to its original position. The capillary is thus transformed back from an analytical cell to a storage space where the sample can be kept for years until the next analysis**.

3. Analysis of the samples

None of the many existing methods of analyzing gaseous mixtures were at all suited for use with the tiny amounts of gas available in the samples taken at high altitudes. There are two possible ways out of this situation: 1) increase the volume of the bulbs in which the samples are collected, 2) increase the sensitivity of the analytical methods without too great a loss of accuracy***. The first way, although apparently very simple, does not lead to the desired result. The bulbs used, with a volume of 3 liters, brought back a sample of less than 1 mm^3 of gas (at N. T. P.) for analysis from altitudes of 95–100 km. If the sampling altitude is increased by only 10–12 km, the volume of the sample will decrease by about one order of magnitude, so that in order to obtain the same volume of 0.3 mm^3, one must increase the volume of the bulb tenfold. Now the use of a glass bulb of

* The atmospheric pressure to which the gas is compressed may be measured with an error of less than 0.5%.

** This method of analysis involves the use of several capillaries. We shall be describing it briefly later on.

*** A third possibility, that of pumping gas into the bulb so that a given volume contains more gas, is attended by great practical difficulties.

capacity 30 liters (or even considerably less) is not possible in rocket investigations for a number of reasons: the difficulty of degassing the large internal surface area of the bulb, the necessity of providing a very large inlet, and the great difficulty of installing the bulb in the rocket and of recovering it intact, etc. Moreover, it is practically impossible to transfer all the gas from such a large bulb (tens of liters) to the analytical apparatus without contaminating it. It is therefore necessary to try the other solution, despite its difficulty: to increase the sensitivity of the existing methods of analysis by devising a new method for the microanalysis of gaseous mixtures which may only amount to fractions of a cubic millimeter (at N. T. P.).

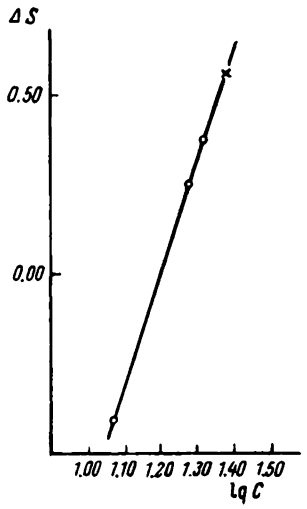

FIGURE 39. Calibration curve for determination of oxygen in the sample

⊙ standard mixtures; X unknown mixture.

We have already described the method used for such analyses outside the Soviet Union in the previous chapter. In this chapter we shall describe the spectroscopic analysis of gaseous mixtures, which was the method we used for analyzing our samples from the upper atmosphere.

Basic Soviet work on spectroscopic methods of investigation of gaseous mixtures, in particular the method of exciting the gas in a high-frequency discharge, was carried out by S. E. Frish and his co-workers /92-97/. The method of spectroscopic microanalysis developed by these scientists allowed them to analyze 2–3 mm^3 of a gasous mixture. We were particularly interested in the special attention paid in this work to the analysis of multi-component mixtures. We therefore sent the first samples which we obtained (at altitudes of 60–80 km) to Frish's laboratory, where they were analyzed by O. P. Bochkova for the three main components: oxygen, nitrogen and argon. After some refinement of the method of spectroscopic microanalysis carried out by us in collaboration with Frish and Bochkova, it was possible to analyze tenths and even hundredths of a cubic millimeter of gas. We further concentrated our attention on improving the excitation conditions in the discharge, the geometry of the discharge tube (capillary) and the stability of the discharge.

Once we worked this method out sufficiently well, our samples from the upper atmosphere were analyzed both in Frish's laboratory and by ourselves. In this chapter we shall describe mainly the work carried out in our laboratories. The work of Frish and his co-workers has already been published in the papers cited above.

For analyzing our air samples, Frish used the method involving a high-frequency discharge without electrodes. This method, which is widely used at present, has for us the decisive advantage over all other methods of spectroscopic analysis in that the electrodes, to which the high-frequency voltage is applied, are outside the discharge tube and therefore do not come into contact with the gas. We thus avoid the very considerable errors which would be caused by reaction of the gas with the surfaces of the metallic

electrodes. The presence of internal electrodes is especially unfavorable in microanalysis, when the portion of gas being analyzed is extremely small. However, despite all its advantages, the discharge method without electrodes is still not free from the general difficulties which attend all methods for the spectroscopic analysis of gases: the necessity of making the results reproducible, of obtaining a sufficiently high accuracy, etc.

The discharge method without electrodes does not differ in principle from the normal gaseous-discharge method. In our work we used the "three-standard" method, which is widely used, e. g., for the spectroscopic analysis of alloys. The basic principle of this method is that the spectrum of the unknown mixture is recorded on the photographic film together with the spectra of three mixtures of known composition. The film is then measured with a photometer, and the results thus obtained used to plot a calibration curve like that of Figure 39 (in which the relative difference in blacking ΔS between two given lines in the spectrum is plotted against the logarithm of the concentration lg C).

The near infrared region of the spectrum, from 7000 to 8000 Å, was used for analyzing our samples for oxygen, nitrogen and argon according to Frish's method. Fortunately, this region contains a strong line of each of the elements involved: O – 7772 Å, N – 7469 Å and A – 7504 Å, which can be recorded and measured with a photometer without difficulty. For the photography of the spectra we used a normal spectrometer with a glass prism (type ISP–51).

The spectroscopic analysis of multicomponent mixtures is the most difficult. A change in the concentration of one component of the mixture can lead to a considerable change in the intensity of the lines of the other components, the precise extent of this change varying from element to element (parallel or nonparallel displacement of the calibration curve). In the following section we shall describe in some detail the ways of increasing the accuracy of the measurements in such cases. We shall only mention here that in our laboratory we managed to determine the concentration of the elements we were interested in with an accuracy of 3–6 %.

4. Spectroscopic microanalysis of gases

The spectroscopic analysis of small amounts of gas involves difficulties which are not met with when analyzing larger amounts. The smaller the amount of gas involved, the more difficult it is to obtain reproducible results; these difficulties will be especially acute when it is necessary to analyze less than 1 mm^3 (at N. T. P.) of a gaseous mixture. In this case, the results are especially strongly influenced by reaction of the excited gas with the glass walls of the tube, leading to instability of the discharge parameters.

When a high-frequency discharge without electrodes is used in a gas, the results of the spectroscopic analysis depend on a number of factors, which may be divided into the following three groups:

A. Factors determining the electron temperature in the discharge: the voltage of the electrodes of the high-frequency generator, the pressure of the gas in the capillary cell, the geometry of the electrodes, the interelectrode distance, the diameter of the capillary, etc.

B. Factors determining the properties of the internal surface of the capillary: the sort of glass used, the "history" of the capillary, the amount

of the mixture to be analyzed, the duration of the luminescence of the discharge, etc.

C. Factors determining the reproducibility of the photographic and photometric procedures: the properties of the film, the exposure time, development, photometry, etc.

The effect of the last group of factors on the analytical results is well known, since it is common to all similar procedures making use of photographic methods. The effect of the first two groups has not yet been finally explained.

The dependence of the electron temperature on various parameters of the discharge has however been investigated by many authors, in particular V. A. Fabrikant /98, 99/ and S. E. Frish /100/; we shall therefore not go any further into this matter here.

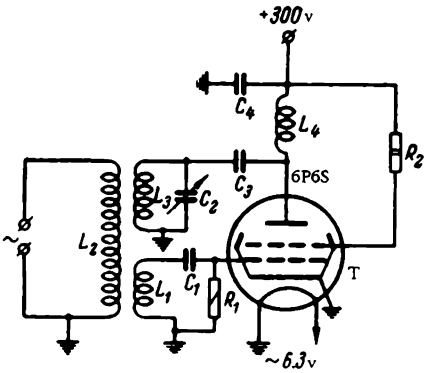

FIGURE 40. Circuit diagram of the small generator

R_1–resistor, MLT 0.5, 35 kΩ; R_2–resistor, MLT 2, 10 kΩ; C_1–capacitor, 40,000 μμf; C_2–variable capacitor, up to 500 μμf; C_3–capacitor, 1000 μμf; C_4–capacitor, 50,000 μμf; T–tube 6P6S; L_1–grid winding, PEL 0.3, 30 turns; L_2–primary winding, LEShO 7 x 0.07, 1000 turns; L_3–anode winding, LEShO 7 x 0.07, 40 turns; L_4–choke V4, PELShO 0.2, 120 turns.

In this section, we shall only deal with some points concerning the influence of the second group of factors, which determine the reaction of the gas with the material of the discharge tube, since it is these factors which largely govern instability of the discharge in gas microanalysis. Sorption effects can considerably change both the composition and the density of the gas, which can lead to a variation in the discharge parameters, in particular the electron temperature. However, before we discuss the conditions for discharge stability, we shall devote a few words to the means we used to excite the spectra.

The small high-frequency generator. Several high-frequency generators have already been developed for exciting discharges in the investigation of gases. Details of the VG-2 generator, produced by the experimental workshop of the NIFI LGU*, are given in the book /96/. We originally used this

* [Nauchno-issledovatel'skii fizicheskii institut Leningradskogo gosudarstvennogo universiteta–Physical Research Institute of the Leningrad State University.]

generator, but its excessive size and needlessly large power, together with the known instability of its operation and its thermal inertia, made us decide to turn to a simpler and more economical generator. At our request, engineer V. I. Makarov designed and constructed a generator which not only worked better than the VG-2, but was also simpler to use and smaller. The circuit diagram of this generator is shown in Figure 40, and a photograph of it in Figure 41. This generator differs from the VG-2 in its "pocket-size" dimensions (which can be reduced even further) and in its

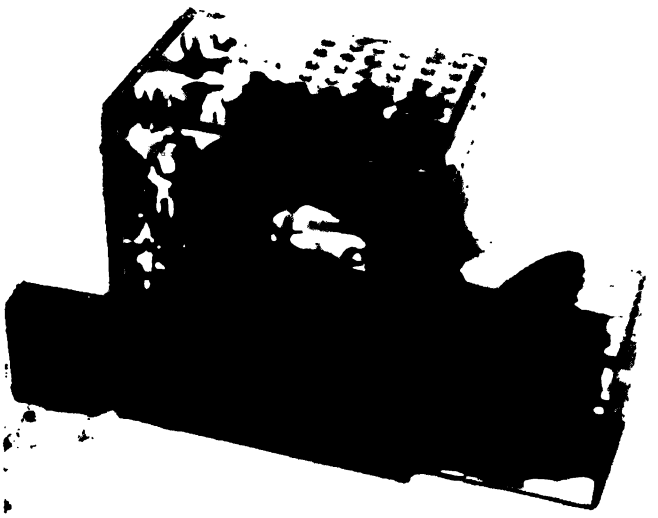

FIGURE 41. The small generator

electrical characteristics: the current in the discharge does not exceed 1.5–2 ma, the voltage of the electrodes is of the order of 2500–4700 V, and the power consumption is 1–2 w. The frequency can be varied from 0.82 to 0.57 megacycles per second, corresponding to a wavelength variation from 370 to 530 m. These characteristics guarantee good ignition of the discharge and reproducible results. It may be mentioned that the low discharge current (1.5–2 ma), which is less by approximately two orders of magnitude than that normally obtained with the VG-2, allows the separate excitation of all the above-mentioned lines of the air samples to be analyzed. Moreover, this reduction of the discharge current considerably lowers the overall gaseous (ionic) temperature of the discharge.

The effect of the temperature of the walls of the discharge capillary. As we have already mentioned, it is possible, by studying and taking into account the second group of factors which influence the stability of the discharge, to increase the accuracy of the analysis of the gas samples. Since this question is not treated fully in the literature as far as we know, we shall give a brief discussion of it here*.

* We shall be publishing papers giving a more detailed treatment of this subject.

The reaction of a gas with the surrounding surface depends on a number of factors. If we assume that the nature of the gas and the surface are constant, the temperature of the wall and of the gas in contact with it are the main factors determining the course of the reaction. This temperature determines the sorption and desorption effects, and also the diffusion of certain gases (hydrogen, helium) through the discharge tube itself (quartz, glass). The author, together with D. A. Mirtova, therefore investigated the equilibrium temperature of the gas-discharge tube system (capillary cell), and the time taken to reach this equilibrium. This investigation was carried out using a thermocouple connected to a sensitive galvanometer. The hot junction of the thermocouple was fixed to the outer wall of the capillary cell, and the cell together with the thermocouple was placed in a vacuum jacket to prevent convection currents from interfering with the temperature of the wall. The wall temperature was measured in this way at various points both in and out of the discharge zone.

Some of the results of these measurements led to the following conclusions:

1) with a given voltage between the electrodes and without a discharge in the capillary cell, clean glass or quartz is not appreciably heated in the high-frequency field of the generator, no matter whether there is gas in the cell or not. The wall is rapidly heated to incandescence if the capillary is dirty on the inside or the outside. The brown film, which is formed on the inside wall of the capillary by the decomposition of grease vapors due to the high temperatures in the discharge, is particularly harmful;

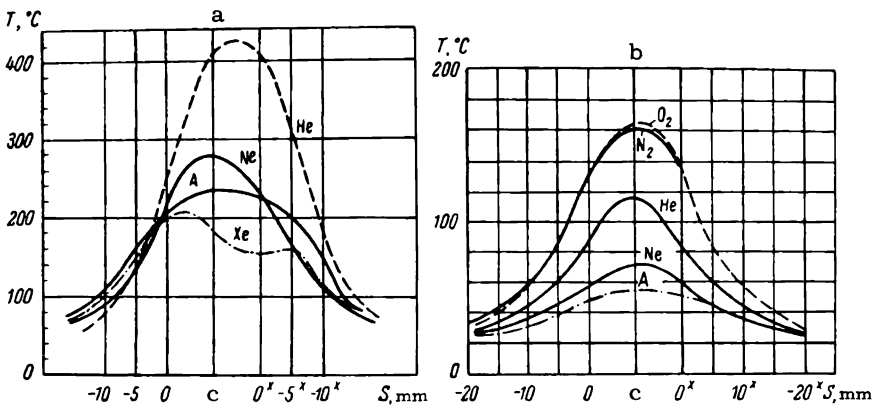

FIGURE 42. Temperature distribution along a (molybdenum) glass capillary in the presence of a high-frequency discharge from the VG-2 generator (a) and the small generator (b)

c—center of discharge region; the zeroes on each side of this represent the positions of the flat electrode disks, which are separated by a distance of 15 mm; to the right and left of these are plotted the distances outside the discharge region.

2) the temperature of the walls increases if a discharge is formed in the capillary cell. The temperature of the gas in the discharge, which determines the temperature of the walls, depends strongly on the nature of the gas in question. Some results are shown in Figure 42. For monatomic gases, the temperature increases with a decrease in the atomic weight. The "coldest" gas in a discharge is xenon, and the "hottest" is helium. The

temperatures of diatomic gases (nitrogen, oxygen) do not differ much, but considerably exceed those of all monatomic gases*. Figure 42 also shows the variation of temperature along the capillary. The maximum temperature is normally found at the center of the discharge region, as long as the latter is not too large. The temperature of the capillary falls off sharply at the ends of the discharge region. Xenon shows a somewhat different picture, with two maxima (one near each electrode) and a minimum near the center of the discharge. The other gases also show a similar picture when the distance between the electrodes is increased to about 35–45 mm. This effect is connected with the thermal conductivity of the gases;

3) the temperature of the capillary wall does not reach its maximum value at once. Even with a thin-walled capillary cell (diameter 0.4 mm), it takes 3–4 minutes (under the chosen conditions), as can be seen from Figure 43;

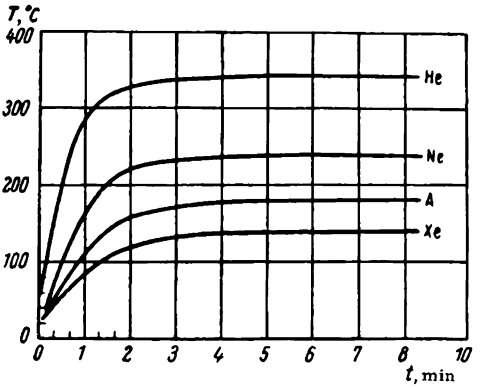

FIGURE 43. Time taken for the temperature of the wall of a (molybdenum) glass capillary to reach equilibrium in the presence of a high-frequency discharge for various gases

The temperature is measured at the middle of the discharge region; the walls of the capillary are 0.5 mm thick, its internal diameter 0.4 mm; the time from the ignition of the discharge is plotted along the abscissa.

4) with given discharge conditions and given geometry of the electrodes and of their separation, the temperature of a quartz capillary always considerably exceeded that of a (molybdenum) glass one;

5) the power of the generator maintaining the discharge has a considerable effect on the wall temperature of the capillary. Comparison of Figures 42a and 42b shows clearly that under optimum operating conditions (discharge glowing most brightly), the VG-2 generator gives a much higher temperature than the small generator described above;

6) the geometry of the electrodes and their separation have a great influence on the wall temperature. Electrodes made of wide metal strip placed in direct contact with the capillary produced a very high wall temperature. Disk-shaped electrodes, with a central hole much larger than the

* This increased temperature of polyatomic gases is apparently largely due to dissociation processes occurring in the discharge.

cross section of the capillary cell, were the most suitable in this respect. The lowest wall temperature is found when the distance between the disks (the length of the discharge region) is minimum.

The above observations allow the most suitable conditions for the analysis of small samples of gas to be chosen. The following recommendations may be made: 1) thin-walled capillaries should be used, with disk-shaped electrodes not touching the capillary and situated the minimum distance apart (in our case 8–10 mm); 2) the spectrum should be recorded after the temperature has reached equilibrium (with thin-walled capillaries, this takes about 3–4 minutes); 3) a low-power generator must be used for exciting the discharge; 4) we must conclude that, contrary to accepted opinion, quartz capillaries are not better than glass ones for the microanalysis of gases by the high-frequency-discharge methods.

The results of our work showed that quartz does not have the expected advantages over glass. In most cases, the use of glass was in fact much to be preferred. When the operating conditions are chosen properly, thin-walled (molybdenum) glass capillaries of diameter 0.5 mm and less can be used for a long time (months) without any noticeable deterioration in the structure of the glass.

Reduction and stabilization of the wall temperature of the capillary cell. However well the operating conditions were chosen for the microanalysis of the gas in the capillary by the high-frequency-discharge method, the temperature of the gas and of the wall of the capillary was quite high and unstable.

In order to reduce and stabilize the temperature, we (in collaboration with A. G. Starkova) tried cooling the capillary cell with a stream of cold air of constant velocity. By this means, we were able to prevent the external temperature of the capillary cell from rising more than 10–15° above the ambient temperature, even with the "hotter" gases like oxygen and nitrogen. This also had its effect on the reproducibility of the results. Table 26 shows

TABLE 26

No. of sample	Difference in blackening ΔS					
	with constant cooling		without cooling		with variable cooling	
	O_2–N_2	A–N_2	O_2–N_2	A–N_2	O_2–N_2	A–N_2
1	–0.24	0.09	0.01	0.05	0.24	0.11
2	–0.28	0.14	0.01	0.04	–0.70	0.11
3	–0.28	0.10	–0.10	0.05	0.75	0.04
4	–0.26	0.11	–0.03	0.04	0.00	0.07
5	–0.26	0.13	–0.02	0.05	–0.39	0.12
6	–0.21	0.10	–0.09	0.08	–0.32	0.17
7	–0.25	0.12	–0.12	0.07	–0.64	0.12
8	–0.28	0.09	–0.08	0.09	0.60	0.09
9	–0.25	0.12	–0.06	0.08	–0.72	0.15
10	–0.25	0.11	–0.03	0.07	0.70	0.12

the results of measuring with a photometer the oxygen (7772 Å), nitrogen (7469 Å) and argon (7504 Å) lines of normal air (the results being expressed relative to the 7469-Å nitrogen line) with constant air cooling, without air cooling, and with variable air cooling of the capillary cell. It can be seen

that the error in determining the reproducibility of the ratios O_2/N_2 and A/N_2 is less when the capillary is constantly cooled than without cooling.

The use of several capillary cells. Apart from the temperature of the gas and of the capillary wall, the "history" of the capillary has a strong influence on the reproducibility of the results (see /96/).

After a discharge has taken place for a long time in the discharge tube, the wall of the tube will be covered with the gas taking part in the discharge. This gas is very firmly attached to the wall of the tube, and cannot be removed by evacuating the tube. When a new discharge is initiated in this tube, with a gas of different composition, the sorbed gas will take part in the discharge and may alter the analytical results. It has so far not proved possible to get rid of this undesirable effect. "Cleaning" the capillary by means of a discharge in some suitable gas does not always give the desired results.

We therefore used the "several-capillary" method, which we have already mentioned above, for analyzing our air samples. The principle of this method consists in recording the spectra of the standard mixtures not in the capillary cell used for the unknown sample, but in other capillaries identical with the first*. For this purpose, each standard mixture is contained at the pressure necessary for the analysis (in practice 7–10 mm Hg) in special sealed vessels. Each vessel is fitted with a side arm terminating in a thin-walled capillary. If this capillary is introduced into the discharge region of the generator, the gas begins to glow. The necessary number of experimental points for the construction of the calibration curve (usually three) are obtained by changing the standard mixture in the discharge region. This solves the problem of the "history" of the capillaries as far as the standard mixtures are concerned.

The problem of the capillary cell in which the unknown samples are analyzed is more difficult. A freshly annealed capillary strongly absorbs certain gases (in particular oxygen) in the presence of a discharge. Therefore, it is not possible to use such capillaries untreated. Since we do not have enough of our unknown samples to use them for "cleaning" the capillary, we must use some gas which is not contained in the investigated mixtures for this purpose. In our case, helium proved to be very suitable. After such a treatment, the "history" of the capillary cell will be simple and standardized enough for all samples of air to be analyzed.

5. The vacuum apparatus

For analyzing the small high-altitude air samples, it is necessary to transfer these samples from the bulbs in which they are contained to the capillary cell, and there they should be compressed to a given pressure. This is done using the special vacuum apparatus shown in Figure 44 /86/.

This apparatus is so designed that the sample does not have to pass through a maze of glass tubing to get to the capillary cell, which would lead partly to contamination, and partly to loss of gas by adsorption on the large area of glass or by getting left behind in "pockets" of the apparatus. The layout of the apparatus is sketched in Figure 45.

* Capillaries cut from the same length can be very similar in shape. In any case, the error introduced by variations in the geometry of the various capillaries is much smaller than the other errors.

The equipment shown here was designed for use with the "single-capillary" analysis method (in which the standard mixtures are introduced into the same capillary cell as the unknown). The pure gases used to make up

FIGURE 44. The vacuum apparatus used for the spectroscopic analysis of the samples

the standard mixtures are contained in separate vessels, and are introduced into the vacuum apparatus via the special mercury closing devices /101/ shown in more detail in Figure 46. These closing devices operate as follows. The gas from one of the vessels can only get into the vacuum apparatus through the narrow capillary 1 which passes through the dividing glass wall 7. The capillary ends in the porcelain cone 2. The top and bottom ends of the capillary are immersed in mercury 8; the top, porcelain-tipped end, however, is immersed only when the glass tube 3 dips into the mercury. To prevent this tube from floating on the mercury, the metal core 4 is sealed into its top. When this tube dips into the mercury, the mercury level rises above the porcelain so that no gas can pass from the vessel in question into the vacuum apparatus. If this tube is lifted, the mercury level falls and exposes the porcelain cone. Therefore the gas can pass through the pores of the porcelain into the vacuum apparatus after making its way through the mercury covering the bottom of the capillary 1.

The solenoid 6 is fixed round the tube 9. When a current is passed through this solenoid, it attracts the steel core 4 of the tube 3, so that the closing device is opened; when the current is shut off, the tube falls again, and

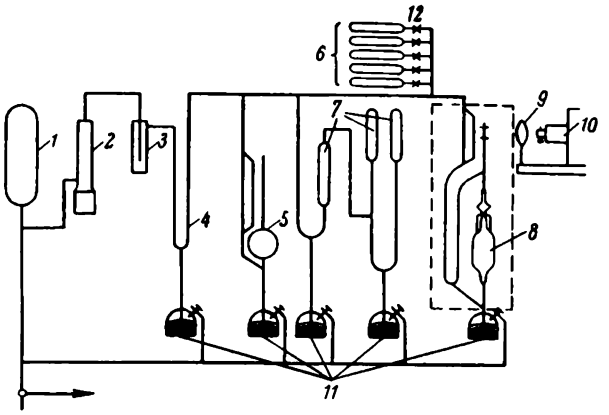

FIGURE 45. Diagram of the vacuum apparatus used for the spectroscopic analysis of the samples

1–backing pump; 2–Langmuir high-vacuum pump; 3–trap cooled by liquid nitrogen; 4–U–tube mercury closing device; 5–McLeod gauge; 6–set of bulbs containing pure gases; 7–mixer; 8–bulb with sample, attached to capillary cell; 9–focussing lens of spectrograph; 10–ISP-51 spectrograph; 11–mercury reservoirs (shortened); 12–remote-controlled mercury closing devices for admitting gas into the apparatus.

mercury covers the capillary 1. If air accidentally gets into the vacuum apparatus, some of the mercury from the lower drop is automatically forced into the capillary, effectively closing the device and thus preventing the air from contaminating the gas in the vessel. When the vacuum apparatus is pumped out, the mercury emerges from the capillary again and the closing device is ready for use. This makes it possible to open the vacuum apparatus without any trouble, which is necessary when the bulb with the sample is being attached to the apparatus.

These mercury closing devices are indisputably better than ordinary "closing" taps. In the first place, they do away with the use of vacuum grease, and in the second place they facilitate the measuring out of the desired quantities of gas. Moreover, they are remote-controlled, which is very convenient for work with vacuum equipment*.

The equipment shown in Figure 45 also includes the mixer 7, which can be used for making up and storing various mixtures. The central part of the equipment, however, is the capillary cell with the bulb 8 containing the sample; this part is surrounded by broken lines in Figure 45, and is shown in more detail in Figure 47**.

As we have already mentioned, the small sample of gas contained in the bulb must not be introduced into a complicated vacuum system. The system

* Our many years of work with these mercury closing devices has confirmed their decided superiority over other types of taps.

** Since most of our samples were investigated in this way, i.e., with the whole bulb attached to the vacuum apparatus, and not just the capillary cell, we shall describe this method here; in any case, the system shown in Figure 45 is used to transfer the gas from the bulb to the capillary.

of connecting tubes shown in Figure 47 is therefore designed so that the gas can be transferred straight from the bulb to the capillary cell. The bulb is sealed on to the vacuum apparatus with its glass "tears" unbroken, as

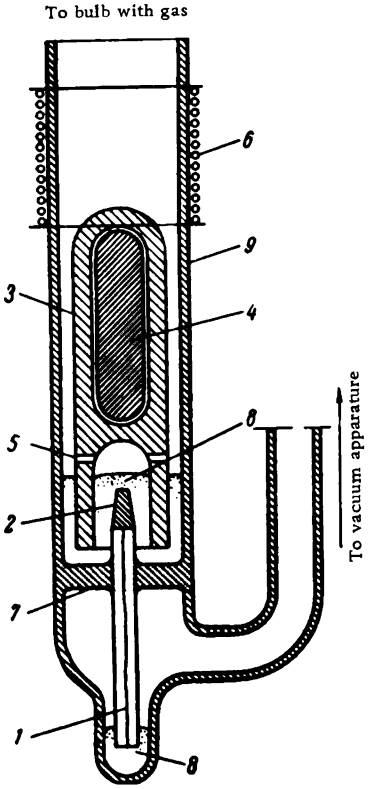

FIGURE 46. Remote-controlled mercury closing device for admitting gas to vacuum apparatus

shown in Figure 47. The vacuum apparatus is then carefully evacuated and degassed, as up till now it has been open. When the degassing is completed, the mercury level is raised to A (Figure 47) and the lower glass "tear" of the bulb is broken by a special weight. The mercury fills the bulb, compressing the gas to just under the upper glass "tear", which is broken when the mercury has reached the level B.

Further compression forces the gas straight into the capillary cell*.

This method of displacing the gas from the bulb by mercury is not so easy to use when the bulb is large. When a thin-walled glass bulb with a capacity of 3 liters is filled with mercury, there is a considerable risk that it will break. This risk was avoided in the following way**. The bulb is first sealed on to the vacuum apparatus in the normal way (see Figure 47). It is then surrounded by a cardboard or tin-plate container of diameter

* Other methods of transferring the gas to the capillary (with the aid of pumps) generally lead either to contamination of the sample or to loss of some gas in "pockets" of the pumping apparatus.

** Suggested by A. A. Baikov.

about 2–3 cm more than the bulb, which is supported by a stand placed under the bulb. The space between the container and the bulb is then filled with a solution of plaster of Paris. When the plaster has set, the bulb can be filled with mercury without any risk. The vacuum apparatus with a bulb protected in this way is shown in Figure 48.

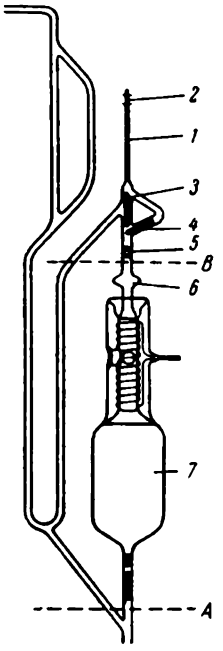

FIGURE 47. The bulb and the capillary cell

1–capillary cell; 2–discharge region; 3–weight for breaking upper glass "tear"; 4–stop for weight; 5–glass "tear"; 6–stopper of tap of bulb; 7–bulb; A–mercury level when the lower glass "tear" is broken; B–mercury level when upper glass "tear" is broken.

When the gas has been compressed to just under the glass "tear" 5 (Figure 47), which is as yet unbroken, and the mercury level has been raised to B, the gas must be strongly cooled to remove all traces of water vapor, carbon monoxide and carbon dioxide which may be present in the vacuum apparatus. A normal cold trap cannot be used in this case, as it would lead to an appreciable loss of the gas sample. We therefore used a "straight" trap, which did not contain any "pockets" in which gas could be lost. This trap is shown in Figure 49. The basic part of this trap is a double-walled glass tube, the space between the walls being well evacuated. This tube is open at both ends. It is sealed into a normal glass tube which forms part of the vacuum apparatus, being situated just below the capillary cell (see Figure 47). A Dewar vessel for liquid nitrogen is sealed round this outer tube in order to cool it strongly. The frozen walls of the outer tube act as a trap collecting the condensed gases. If the inner "Dewar tube" were not there, the mercury would be rapidly frozen on coming into contact with the cold wall of the tube, and would form a solid plug, preventing access to

FIGURE 48. The analytical apparatus with a reinforced bulb. On the right are shown two thin-walled glass bulbs reinforced with plaster of Paris

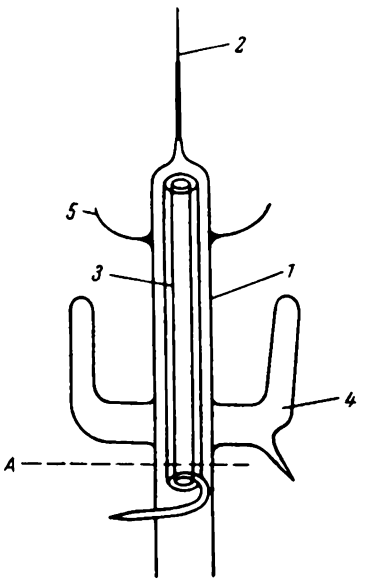

FIGURE 49. Sketch of "straight" trap

A–level reached by mercury before cooling the gas; 1–outer tube; 2–capillary cell; 3–inner "Dewar tube", through which the mercury can still pass freely when the walls of the tube 1 are cooled; 4–external Dewar vessel for cooling tube 1; 5–glass screen, preventing cold liquid nitrogen vapor from reaching the upper end of the tube 1.

the capillary cell. Thanks to the presence of the Dewar tube, the plug of solid mercury is only formed between the wall of the outer tube and the inner Dewar tube. The inside of the inner Dewar tube does not freeze, but remains free for the passage of mercury. The mercury flows over the top of the tube, filling the trap, and rises to the capillary cell, collecting there all the gas which has passed through the trap. The pressure in the capillary is adjusted to the desired value, the high-frequency voltage is applied to the electrodes round the cell, and the gas in the cell begins to glow. The spectrum of this discharge is recorded with a spectrograph, and the gas sample can then be analyzed.

6. Experimental results

Between 1951 and 1957 we did a great deal of work on collecting air samples at high altitudes. These samples were analyzed by us in collaboration with O. P. Bochkova. The samples were collected and analyzed by the methods which we have described above. Not all the experiments were successful; Table 27 therefore only gives the results of those analyses for which the experimental accuracy is not in doubt. The samples were collected in the middle latitudes of the European territory of the Soviet Union, preferably in the spring and summer, and during the morning (local time).

TABLE 27

Height, km	Pressure inside bulb, mm Hg	Composition of sample, vol. %			Height, km	Pressure inside bulb, mm Hg	Composition of sample, vol. %		
		O_2	N_2	A			O_2	N_2	A
65	$1.7 \cdot 10^{-1}$	19.0	80	0.91	82–85	$4 \cdot 10^{-3}$	24.5	74	0.77
75–80	$2.0 \cdot 10^{-2}$	21.0	78	0.93	82–85	$3.7 \cdot 10^{-3}$	20.5	78	0.79
75–80	$2.5 \cdot 10^{-2}$	21.0	78	0.93	82–85	$4.4 \cdot 10^{-3}$	19.0	80	0.91
80	$1.1 \cdot 10^{-2}$	21.5	78	weak	85	$3.7 \cdot 10^{-3}$	21.0	78	0.86
80	$1.0 \cdot 10^{-2}$	19.0	80	0.86	85	$3.2 \cdot 10^{-3}$	21.0	78	0.90
80	$1.5 \cdot 10^{-2}$	22.0	77	0.87	85	$3.4 \cdot 10^{-3}$	21.0	78	0.88
80	$8.0 \cdot 10^{-3}$	23.0	76	0.90	95	$1.2 \cdot 10^{-3}$	21.5	77	0.76

The following conclusions can be drawn from the results of Table 27: there is no appreciable separation between oxygen and nitrogen up to an altitude of 95 km; the amount of the heaviest gas argon at altitudes of 85–95 km is less than at the Earth's surface.

Although the decrease in the argon content with height is slight, it can nevertheless be concluded that diffusive separation does operate at altitudes of about 100 km.

The present data on the composition of the upper atmosphere gives a more unified picture than we had three years ago /86/. It is true that there is still some disagreement between experiment and theory /102-104/, but as far as isolated experimental results are concerned, in particular the results obtained by use of radio-frequency mass spectrometers, the new work yields results in agreement with theory. Moreover, critical study of

the earlier work reveals defects in it, which means that the discrepancies found at that time need not be taken too seriously.

Some authors have recently cast doubt on the very essence of the sampling method /105, 106/. We must therefore give a detailed account of these objections and misgivings here.

E. G. Shvidkovskii /106/, for example, quite rightly showed that when the sampling method is used, the correct interpretation of the results depends on an accurate knowledge of the angle between the velocity vector of the rocket (container) and the axis of the bulb's inlet tube at the moment of sampling. It is very difficult to determine this angle of incidence. However, the way in which we carried out our measurements with the container largely avoids this difficulty. Also a help in this respect are the low velocity of the container at the moment of sampling – about an order of magnitude less than the thermal velocity of the molecules (the container is then at about the peak of its trajectory) – and the situation of the bulbs within the open compartment; the bulbs are placed so that their inlet tubes are not directly in a current of air.

The essence of the objections raised by Martin /105/ is that the "gravitational separation" observed by Paneth was in fact the result of distortions which are due to measurements being performed in flight. In particular, the length of the inlet tube of the bulb (25 cm) could lead to forced separation of the gases flowing into the bulb under Knudsen conditions. He also showed that the high velocity of the rocket at the moment of sampling (several times the velocity of sound) leads to a difference between the pressure in the bulb and the ambient pressure, which also gives a possibility of forced separation.

The calculations carried out by Martin, making use of the details of the American experiments (bulb volume, diameter and length of inlet, rocket velocity, moment of sampling, etc.), support his assumption of forced separation at the moment of sampling. However, Martin's assumption of forced separation does not apply to our experiments, which differed widely from those of the Americans. In the first place, our small bulbs had practically no inlet tube (the length of the inlet opening in the tap did not exceed 1 cm), and in the second place the velocity at which the samples were taken did not exceed 30-50 m/sec (peak of the trajectory)*. The pressures inside and outside the bulb were therefore more or less equal, indicating that the pressure in the bulb had reached equilibrium. In the third place, the aerodynamic conditions of our measurements, with our small, relatively slow-filling container, differed very considerably from those of the American work in the rocket itself. The objections which Martin made concerning the American experiments therefore hardly apply to our work.

Finally, we should mention that our results are in good agreement with those of E. A. Wenzel et al. /107/. As an illustration of this, we give a graph (Figure 50) taken from Wenzel's publication which gives the results of American work on the gravitational separation of nitrogen and argon by the sampling method (black dots) and using the radio-frequency mass spectrometer (open cirlces), compared with our results (squares). In this graph, the separation coefficient r (if $r = 1$, there is no separation) is plotted against the height.

* This once more shows the superiority of the container over a rocket for these purposes: when working with rockets, the investigators had to use high velocities to "escape" from the cloud of gas. For the "gasless" container this was not necessary.

If we consider that the time and place (high, low and medium latitudes) of sampling differed very considerably for the American experiments and ours, the agreement between the results must be regarded as good. It is

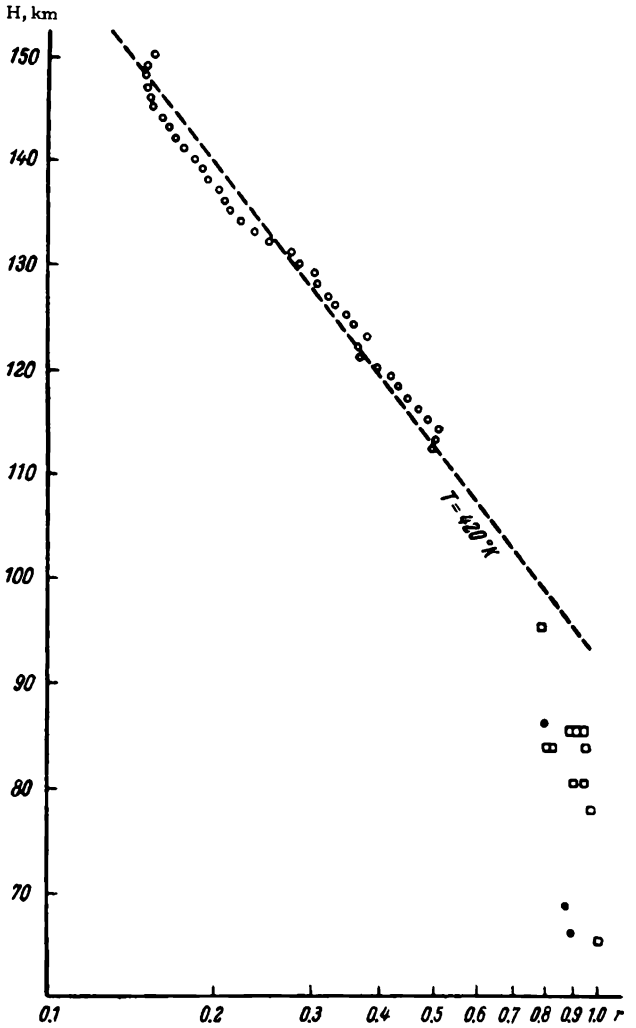

FIGURE 50. The gravitational separation of the gases nitrogen and argon

highly improbable that this agreement is fortuitous, especially as the two sets of experiments differ not only in the sampling method but also in the method of analysis. We may therefore conclude that the gravitational separation of nitrogen and argon at altitudes of about 100 km, observed by both American and Russian workers, does in fact exist.

Chapter V

INVESTIGATIONS OF THE COMPOSITION OF THE UPPER ATMOSPHERE USING ROCKET-BORNE RADIO-FREQUENCY MASS SPECTROMETERS

Introduction

In the previous chapters we have tried to give as complete as possible a survey of the investigations of the composition of the air by the classical method in which a sample is taken and analyzed in a laboratory back on Earth. In this account we have hardly touched on the question of the investigation of the formation of unstable gases – chemically active atoms and molecules formed at high altitudes. Nor have we mentioned the investigation of the ionic composition of the ionosphere. While these chemically active atoms and molecules, and ions, are formed in negligible amounts in the lower layers of the atmosphere, in the upper layers they play an important, if not the main, part in determining the chemical composition of the Earth's atmosphere.

Until a few years ago, these two subjects (the investigation of the unstable molecules and of the ions of the ionosphere) would not have been included in a review article in this field, for the simple reason that no direct measurements of the formation of these substances in the upper atmosphere were being made. Information on the formation and disappearance of such particles in the upper atmosphere (mostly of a qualitative nature) was obtained by investigation and identification of the spectra of the aurorae and of the night airglow. The information thus obtained was often highly uncertain, and no definite conclusions could be drawn about the quantitative distribution of these substances in the atmosphere, leaving ample room for the postulation of contradictory hypotheses.

The position has now suddenly changed. The new means of ascent (high-level experimental rockets and artificial satellites) and the use of radio-frequency mass spectrometers has made it possible to obtain a complete picture of the distribution in space and time of all the components of the upper atmosphere (chemically stable gases, chemically unstable gases, and ionized gaseous particles).

Keeping to a chronological presentation, we shall in Chapters V and VI describe the above-mentioned investigations, which at present seem to be completing our knowledge of the Earth's atmosphere.

1. Characteristics of the composition of the upper atmosphere

The upper layers of the Earth's atmosphere are exposed to electromagnetic (ultraviolet, X-ray) and corpuscular radiation from the Sun, to

cosmic radiation and (to a certain extent) to meteorites, a constant stream of which "invade" the Earth's atmosphere.

Possessing enormous stores of energy, the above-mentioned agents enter into various reactions with the molecules of the atmosphere, often splitting them into single atoms. The upper atmosphere therefore contains certain amounts of "debris" from "broken-down" molecules.

In the first place we have oxygen atoms (O), since the oxygen molecules are very easily dissociated by the shortwave radiation from the Sun. These active atoms can then enter into chemical reaction with the surrounding molecules, forming new compounds like NO, N_2O, etc.

Nitrogen atoms are present in much smaller quantities, as the nitrogen molecule does not dissociate so easily. Apart from dissociation, the above-mentioned agents cause considerable ionization of the particles which they encounter, leading to the presence of ions such as NO^+, O_2^+, O^+, N^+, etc., in the atmosphere*.

The particles formed in this way can collide with one another or with other particles in the atmosphere, giving rise to new, more complicated compounds like O_3, NO, OH, N_2O, etc.

Disregarding the theory of photochemical reactions**, we shall now describe by way of example a number of elementary processes leading to the production of "new" particles in the upper atmosphere.

Oxygen molecules dissociate very easily and directly under the influence of solar radiation in the wavelength range from 1751 to 1200 Å (the Schumann-Runge continuum)

$$O_2 + h\nu \rightarrow O(^1p) + O(^1D).$$

The situation is different with the most common molecules of the atmosphere, nitrogen. No direct process leading to the dissociation of nitrogen molecules into atoms is known to occur in the upper atmosphere. The most probable process in this case is one of dissociative recombination:

$$N_2^+ + e \rightarrow N(^2p) + N(^2D) \quad \text{(Mitra)},$$

following the photoionization of a neutral molecule of nitrogen

$$N_2 + h\nu \rightarrow N_2^+.$$

It is considerably more difficult to follow the formation of complex molecules, since the same end product may be formed by way of different reactions. For example, nitric oxide can be formed by a triple collision reaction:

$$O + N + M \rightarrow ON + M,$$

where M is a "third body", which serves to carry off the excess energy. It can also be formed by means of the reaction

$$N + O_2 \rightarrow NO + O \qquad \text{(Nicolet)}.$$

Once formed, the NO is rapidly removed by reactions like

$$NO + N \rightarrow N_2 + O$$

* Negative ions are rarely formed in the Earth's atmosphere. They have no appreciable effect on the properties of the upper atmosphere, and we shall not consider them here. Molecular positive ions can also be formed by photochemical reactions.

** At the present time, many investigators are carrying out thorough theoretical, and to a lesser extent practical, work on the problems of elementary processes in the upper atmosphere.

There are large amounts of the hydroxyl radical OH in the upper atmosphere, which is formed and disappears much like NO. The following two reactions have been suggested as the main sources of OH:

$$O_3 + H \rightarrow OH' + O_2 \text{ ozone-hydrogen hypothesis,}$$
$$O_2 + H \rightarrow OH' + O \text{ oxygen-hydrogen hypothesis*.}$$

The hydroxyl radicals formed in this way enter into further reactions on collision with other molecules, like NO, thus ending their independent existence. Molecules of ozone, O_3, water H_2O and many different oxygen-nitrogen compounds may be formed and broken down in similar ways in the upper atmosphere**.

The atoms and molecules formed in this way may be either neutral or ionized; moreover, part of them will be excited to various degrees.

As we have seen, none of these substances (except, of course, "terrestrial" water) is found in appreciable quantities in the lower atmosphere. Because of their chemical reactivity, they are specific products of the upper atmosphere, where they are "born" and "die". The lifetime of such chemically unstable substances is determined by two factors: their individual physicochemical properties, and the height at which the molecule (or atom) in question is formed. Atoms and monatomic ions can only change state on collision with other particles in the atmosphere (apart from ionization). Therefore, the higher up in the atmosphere they are formed the longer their life, since there is then less risk of collisions which can return the atom (ion) to the chemically (electrically) stable state which characterizes the constituents of the lower atmosphere. The fate of diatomic and polyatomic compounds (O_2, O_2^+, N_2, N_2^+, NO^+, OH, O_3, etc.) is more complicated. Their lifetime must however be shorter than that of monatomic substances, since their state can be changed not only on collision but also under the direct influence of extraterrestrial agents (quanta of a given energy).

The above-mentioned factors together determine the "life" of the upper atmosphere, the course of which is regulated on the one hand by external factors (irradiation) and on the other hand by collisions between the different particles. As a result of this a dynamic equilibrium is established in the atmosphere, determining at each height the concentration of the substances formed there. This equilibrium is fairly mobile, since one of the factors which determines it — the ultraviolet radiation from the sun — is variable. A change in solar activity, leading to a variation in the amount of ultraviolet radiation emitted by the Sun, will have a direct effect on this equilibrium, shifting it one way or the other.

The disappearance of the Sun below the horizon each day will have a particularly marked effect on the "life" of the upper atmosphere. As night falls, the radiation source causing the dissociation and ionization of molecules disappears, and processes tending to return these particles to a stable state predominate***.

* The prime indicates that the radical is in an excited state.

** About fifty oxygen-nitrogen compounds are known to chemistry, although of course the probability that any one of these compounds will be formed in the upper atmosphere is immeasurably less than the probability of formation of the compounds mentioned in the above examples.

*** At altitudes exceeding 700-1000 km, a great role in the "life" of the atmosphere may be played by "terrestrial" radiation (from the radiation belt) recently described by Soviet and American investigators.

It goes without saying that in the lowest layers of the atmosphere, into which the agents causing the dissociation of molecules in general do not penetrate and collisions between the molecules are frequent, finally leading to the production of chemically stable and electrically neutral O_2 and N_2 molecules, the inner "life" of the atmosphere "dies off", leading to our usual picture of an atmosphere consisting of a physical mixture of known gases.

It thus follows that the field of activity of the investigator studying the composition of the atmosphere is widened at altitudes higher than 80–95 km, and it becomes more difficult to obtain a clear theoretical insight into the problem of the variation of the composition with height.

At these high altitudes, even in the complete absence of mixing, the relative distribution of the various gases at different heights is not determined by Dalton's law alone. The "life" of the upper atmosphere described above leads to considerable departures from the distribution predicted by Dalton's law. The distribution of gases in these regions of the atmosphere is in fact determined by the simultaneous action of at least four factors — gravitation, diffusion, dissociation and photochemical reactions.

For the construction of a theory describing the real distribution of the gaseous particles in the atmosphere, we need reliable experimental information about all the components of the upper atmosphere at various altitudes. The possibility of obtaining such information was provided by the use of the radio-frequency mass spectrometer.

2. The use of the radio-frequency mass spectrometer for investigating the upper atmosphere*

The classical method of investigating the composition of the atmosphere by means of taking samples in sealed bulbs, which completely solved the problem of the "normal" composition of the atmosphere, up to altitudes of about 100 km, proved completely inadequate for dealing with this new problem of investigating the unstable atoms and molecules and also the ions of the upper atmosphere.

When trapped in a sealed vessel, all unstable substances (O, N, NO, OH, etc.) and also various ions very quickly recombine with each other and collide with the walls of the vessel, forming stable molecules of O_2, N_2, H_2O, the original substances thus being lost for analysis. The investigation of the composition of the "living" atmosphere must thus be based on an entirely different method, allowing the gas to be analyzed directly during the flight without its composition being changed from the original state. One of the most suitable devices which might be used for this purpose is clearly the mass spectrometer.

The technique of mass-spectrometric analysis has been brought to a high pitch of perfection, and is one of the best analytical methods available at present. However, far from all mass spectrometers are suitable for use in rocket investigations of the atmosphere.

The normal magnetic mass spectrometer, which gives an enormous resolving power, great sensitivity and high analytical accuracy, is not

* This section is largely based on the paper written by the author together with V. G. Istomin /122/; a detailed description of the apparatus is given in the paper /130/.

suitable for the above-mentioned purpose. Like all equipment mounted in the rocket, the mass spectrometer must be fully automatic and have as low an inertia as possible. Moreover, the apparatus must be designed to meet a whole series of specialized demands: it must have great mechanical stability, and be insensitive to large overloads and to vibration; it must be able to withstand brief but considerable temperature increases, and be able to work under high-vacuum conditions, etc.

The analyzer of the magnetic mass spectrometer consists of an ion-optical system, the main components of which are a magnet and a series of slits and diaphragms for forming and limiting the ion beam in the apparatus. As a result of this, the size and weight of the apparatus are quite considerable, and the apparatus needs careful regulation and adjustment before it works properly. Another trouble is the extremely small ion current received by the collector of the magnetic mass spectrometer. The amplification of small direct currents is attended by considerable difficulties, one of which is the large time constant of the equipment as a whole, which in its turn places limitations on the scanning rate of the mass spectra. This explains why, after unsuccessful trials of a magnetic mass spectrometer in rockets (in the USA), such experiments were stopped for a while.

Apart from the magnetic type, there are a considerable number of other types of mass spectrometer which do not use a magnetic field in the ion analyzer. One of these is the radio-frequency mass spectrometer, whose analyzer uses an axial electric field /108/. One such apparatus has been

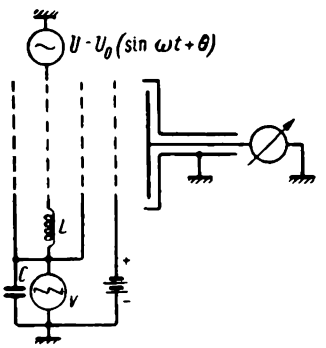

FIGURE 51. Simplified circuit diagram of the tube of the radio-frequency mass spectrometer

described by Bennett /109/. This apparatus, while giving an adequate resolving power, can be made a tenth of the weight of the magnetic mass spectrometer, works faster and gives a collector current which exceeds that of the magnetic mass spectrometer by 2-4 orders of magnitude /110/. Another important point about this apparatus is that no mechanical adjustments have to be made during setting and operation. The disadvantage of the radio-frequency mass spectrometer compared with the magnetic type is its low resolving power; but its resolving power has nevertheless been found to be sufficient for solving a number of geophysical problems.

In the Bennett-type radio-frequency mass spectrometer the ions are sorted according to their velocities. The main component of this apparatus

is the mass-spectrometer tube, a vacuum tube of special design with a large number of plane-parallel grids.

Let us consider the simplified circuit diagram of this tube (Figure 51). A negative saw-tooth accelerating voltage V is applied to the system consisting of three parallel, equidistant grids. In addition, a high-frequency alternating voltage $U = U_0 \sin(\omega t \pm \Theta)$ is applied to the middle grid; the amplitude of this voltage is small compared to the accelerating voltage ($U_0 \ll V$). An ion passing through this system of grids with a certain velocity, which depends on its mass and on the instantaneous value of the accelerating voltage, will gain or lose a certain amount of energy. It can be shown /109/ that the maximum energy is extracted from the high-frequency field of such a three-grid system only by an ion which enters at a certain definite phase of the high-frequency voltage and passes through the system with a certain velocity v_0. As the accelerating voltage is varied with a saw-tooth waveform, this optimum velocity changes so as to correspond in turn to all ionic mass numbers within a certain range.

If now a fourth grid with a suitable positive (retarding) voltage is placed in the path of the ions, this grid can stop all the ions except those which have extracted the maximum amount of energy from the high-frequency field, i. e., those which passed through the system with the optimum velocity. Since the velocity of the ion depends on its mass and on the accelerating voltage, knowing the value of the optimum velocity for a given grid system and the value of the accelerating voltage we may calculate the mass of the ions passing through the potential barrier of the fourth grid and reaching the collector. The ion current of the collector may be amplified and fed to some suitable recording device. The recorded ion current will show a number of peaks, each one corresponding to ions of a certain mass. The mass of an ion is related to the accelerating saw-tooth voltage as follows:

$$M = \frac{0.266}{s^2 f^2} V, \qquad (1)$$

where M is the mass number of the ion, V is the value of the saw-tooth accelerating voltage in volts, s is the distance between grids in cm, and f is the frequency in megacycles per sec.

The system described above does not work adequately in practice. Therefore in the Bennett radio-frequency mass spectrometer the ion analyzer consists of three sections of three grids each, separated by "drift spaces". The length of the drift spaces is chosen so that the transit time of ions of optimum (synchronous) velocity v_0 across each drift space is equal to a whole number of periods of the high-frequency voltage. This ensures that an ion entering the first section at the optimum phase of the high-frequency voltage will reach the following two stages at the same optimum phase. The length of the drift space is expressed as the number of periods of the high-frequency voltage (the number of cycles) taken by an ion to cross it (at optimum velocity). Different designs of the analyzer of mass spectrometers of this type may have drift spaces of different lengths. For example, there are the 9–7-cycle and the 5–9-cycle versions. It can be concluded on the basis of the published data that the 7–5-cycle tube is one of the best as regards resolving power.

The complete circuit diagram of the 7–5-cycle mass-spectrometer tube is shown in Figure 52. The electrons emitted by the hot cathode are

accelerated by grid 1, and ionize the gas contained in the tube on their way from grid 1 to grid 2. The ions thus formed are extracted from the ionization space and accelerated by the constant negative potential on grids 3 and 4, and by the saw-tooth potential of the analyzer grids 5-13. A bias potential is applied to the drift spaces A and B, to compensate for a certain increase in the ion velocity produced in the second stage of the analyzer. The

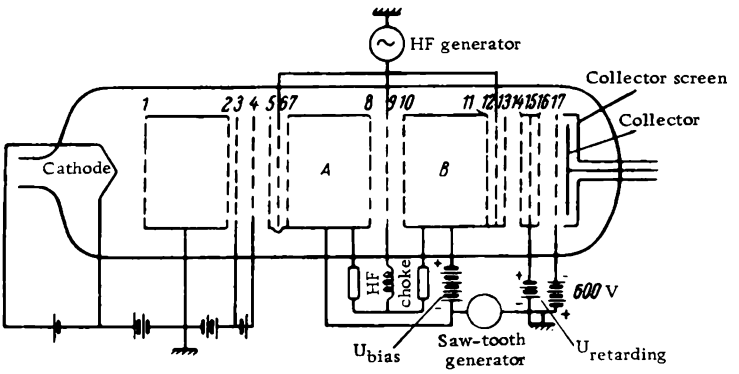

FIGURE 52. Circuit diagram of the 7–5–cycle tube of the radio-frequency mass spectrometer

group of grids 14–16 are placed after the analyzer. These are given a positive, retarding potential. The last grid, 17, has a high negative voltage in order to suppress secondary electrons which may be emitted from the various grids of the tube or from the collector.

Parameters and range of application of the apparatus. The radio-frequency mass spectrometer may be used for analyzing both the neutral and the ionized gases in the Earth's atmosphere. When the apparatus is used to investigate the ionic composition of the atmosphere, the ion source is not necessary as its function is already fulfilled by the ionosphere.

The radio-frequency mass spectrometer with a 7–5-cycle tube has a mass resolution of about 20–25*.

In the present case the resolving power of the apparatus is determined with reference to the base of the peak. A resolution of 25 thus means that the apparatus can give a complete separation between, for example, mass numbers 24 and 25.

The range of masses for which the apparatus can be used is determined (see equation 1) by the dimensions of the analyzer (the distance between the grids in each three-grid section), the operating frequency and the interval through which the accelerating voltage is varied. For example, the apparatus described by Townsend /110/ covered the range from 5 to 48 atomic mass units.

* We may remind the reader that the resolving power (resolution) of the mass spectrometer may be expressed by the ratio

$$R = \frac{M}{\Delta M},$$

where M is the mass number corresponding to the ion-current peak in question and ΔM is the width of the peak in mass-number units, measured at a given level (half-way up the peak, at its base, etc.).

An important parameter of the apparatus is the time needed to produce a mass spectrum. For the radio-frequency mass spectrometer this time is about 1 sec, and can easily be reduced if necessary. This property of the apparatus is very important when measurements have to be made from swiftly moving objects.

The range of application of a radio-frequency mass spectrometer of the type described here is limited not only by the mass numbers involved but also by the height at which the mass spectrometer can still give reliable results. The range of altitudes at which the present radio-frequency mass spectrometers can be used for analyzing the neutral components of the atmosphere is not large: the lower limit is 100–105 km, and the upper limit 200–250 km. These limits are determined by the physical operating conditions of the apparatus in rarefied gases: the mean free path and the concentration of the ions produced by the ionization of the neutral gas under investigation in the apparatus.

If the apparatus is to work normally, the mean free path in the gas under investigation must not be less than the linear dimensions of the analyzer (10–15 cm). The concentration of ions of the gas under investigation must be large enough to give an ion current which can be accurately amplified; it has apparently been found in practice that if the ion source gives a concentration of about 10^3 ions/cm^3, then reliable measurements can still be made.

The situation is somewhat different when the radio-frequency mass spectrometer is used to analyze the ions naturally present in the atmosphere. In this case, the lower operation limit of the apparatus remains the same (100–105 km), but the upper limit is considerably higher (1000 km or more). This is because when the mass spectrometer is used to analyze the ions naturally present in the atmosphere, there is no need for artificial ionization of the surrounding gas. The natural ionization provides a sufficient concentration of ions up to very high altitudes (more than 1000 km).

Much work has been done on the development of the radio-frequency mass spectrometer, and at present the altitude range in which it is used is growing rapidly.

3. American investigations on the neutral composition of the atmosphere

The first Bennett-type radio-frequency mass spectrometer for investigating the composition of the upper atmosphere was used by Townsend in 1952. Between 1952 and 1956, the USA Naval Research Laboratory fitted thirteen high-altitude rockets with this apparatus, but only two of the thirteen flights were successful. Such a high percentage of failures was due to the great complexity of rocket experiments in general and, in particular, to the complexity of experiments involving the use of mass spectrometers. It is therefore hardly surprising that so far, despite the paramount importance of this work, only four successful ascents have been made in the USA for investigating the neutral composition of the upper atmosphere. We shall now proceed to describe these ascents.

The first successful ascent in this series was that of the Aerobee NRL–13, which took place in the night of 12 February 1953 from the White Sands proving ground, New Mexico, at 0 hr 09 min. (Mountain Standard Time,

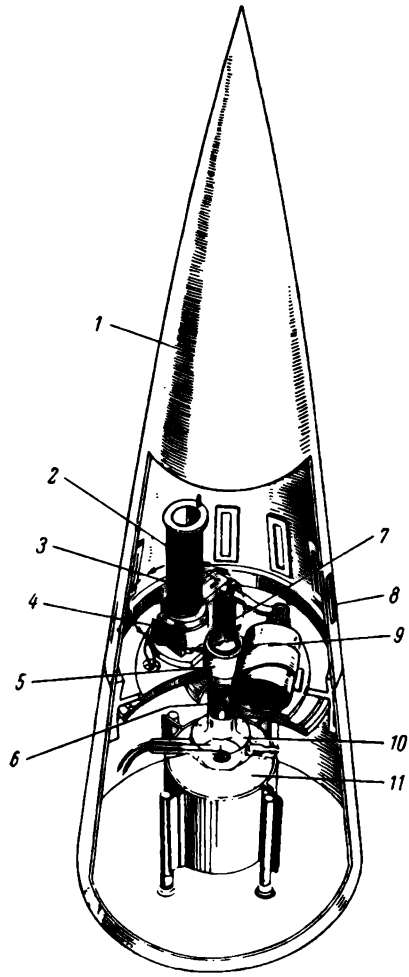

FIGURE 54. Arrangement of tube in rocket

1–rocket nose cone (not jettisoned); 2–locking device; 3-spring which drives hammer; 4-micro-switch; 5-annular seal; 6-bellows; 7-glass cap; 8-window slit; 9-solenoid; 10-radio-frequency mass-spectrometer tube; 11-foam-rubber shock absorber.

FIGURE 53. Three-stage glass mass-spectrometer analyzer tube

1–glass cap with getter; 2–collar for fixing tube in rocket; 3–electrical leads of tube

meridian 105°) /111/. The rocket was fitted with a three-stage glass mass-spectrometer tube, shown in Figure 53. This tube was first thoroughly degassed in a high-frequency oven and sealed at high vacuum. In order to remove as much as possible of the residual gas from the sealed tube, a getter was evaporated on to the top glass cap (Figure 53). The tube thus prepared was then placed in the nose compartment of the rocket. The tube was fixed in place in the rocket by means of metallic and rubber collars, which also served to divide the nose compartment into two parts, hermetically separated from one another: the upper, containing the inlet of the mass-spectrometer tube and the mechanism for opening this inlet at the right time, and the lower, containing the tube itself, electronic equipment, a telemeter and the power-supply unit. The division of the nose compartment is shown in Figure 54. Figure 55 shows an external view of the

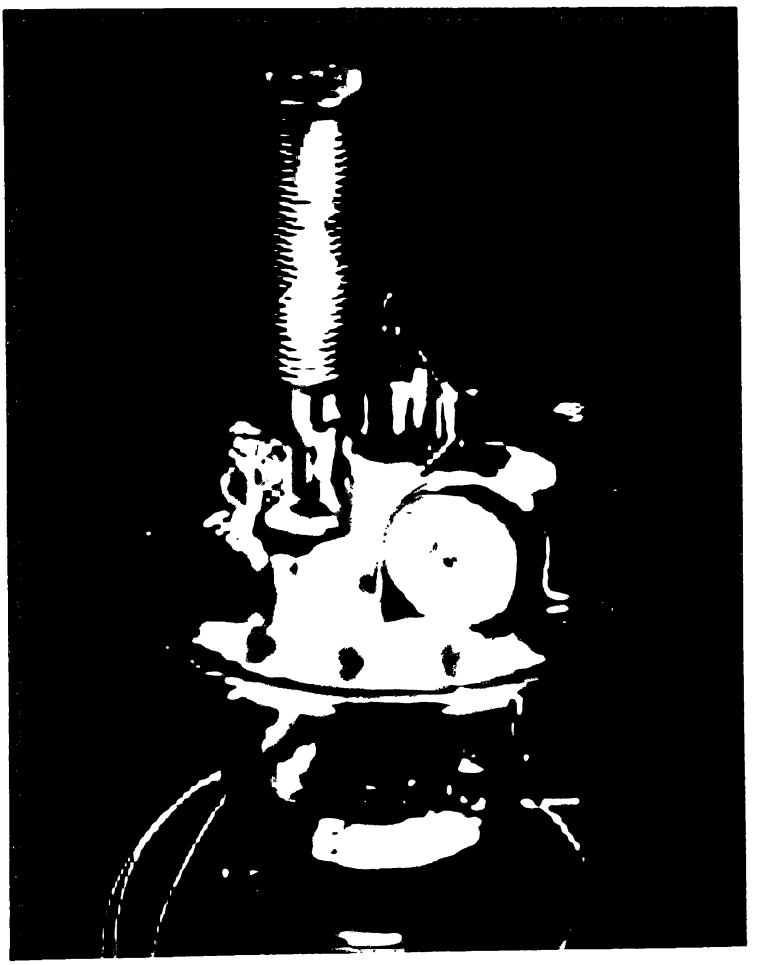

FIGURE 55. The opening mechanism

opening mechanism. In this figure the following can clearly be seen: the spring which drives the hammer, the solenoid which frees the hammer at the right time, and the cap of the mass-spectrometer tube which is to be broken. The compartment of the Aerobee NRL-13 containing the opening mechanism communicates with the atmosphere by means of a number of narrow slits cut in the rocket's shell (Figure 54). All the data obtained by the mass spectrometer were transmitted back to Earth by a special telemetering system, which allowed high-frequency transmission of the details of the mass spectrum (channel with 1250 signals per second). The mass spectrometer used in the ascent on 12 February 1953 covered the mass range from 6–54 atomic units, with a resolution of 1/30 [sic].

Results of measurements. All the measuring equipment in the Aerobee NRL-13 worked properly during the flight. A total of 172 mass spectra were obtained during the ascent from 100–137.3 km and during the descent from 137.3–95 km. The spectrograms showed a large number of peaks, some of which were due to gases in the atmosphere and some to stray gases emitted from the rocket. The recorded peaks corresponded to the mass numbers (in atomic mass units — a. m. u.) 44, 43, 42, 41, 40, 39, 38, 32, 31, 30, 29, 28, 27, 26, 25, 19, 18, 17, 16, 15, 14, 13, 12. The authors divided the peaks into four groups.

The first group contained peaks corresponding to gases present in the undisturbed atmosphere: argon (40), molecular oxygen (32), molecular nitrogen (28), atomic oxygen (16) and atomic nitrogen (14). A characteristic feature of this group was that the measured heights of the ion-current peaks were symmetrical with respect to the highest point reached during the flight.

The second group of peaks (17, 18 and 44) and the third group (15, 25, 26, 27, 30, 39, 41, 42 and 43) were assigned by the authors to the cloud of gas emitted by the rocket, This cloud had no direct relation with the gases of the atmosphere proper.

The fourth group consisted either of peaks of very weak intensity (12, 13, 31, 38) or unidentified peaks (19, 29).

The main result obtained by this ascent, in the authors' opinion, was that gravitational separation of the atmospheric gases nitrogen and argon was not observed up to an altitude of 137 km; the authors considered that the mass spectrometer was sufficiently accurate to justify drawing this conclusion.

Ascent of the rocket Aerobee-Hi NRL-48 in the Arctic

The next successful ascent of a radio-frequency mass spectrometer for analyzing the neutral gases of the atmosphere did not take place until nearly four years after the flight of the Aerobee-13. The new rocket, the Aerobee-Hi NRL-48 was launched from Churchill (Manitoba, Canada) on 20 November 1956 at 2321 hours (Central Standard Time), and carried a payload of 64 kg to an altitude of 251 km /112/. During the time which had passed since the ascent of the first mass spectrometer, not only the rocket but also the mass spectrometer had undergone further development; the latter

FIGURE 56. Four-stage glass mass-spectrometer tube

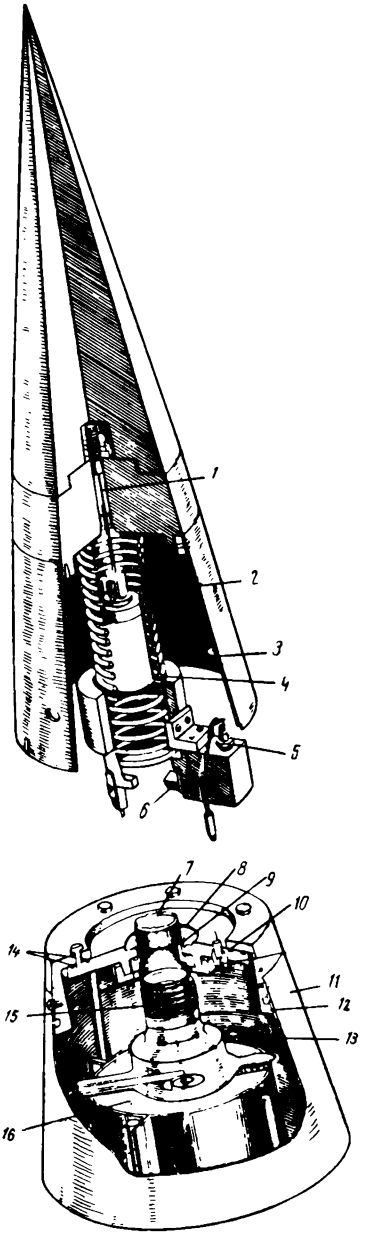

FIGURE 57. The mechanism for opening the mass-spectrometer tube

1–flexible cable; 2–Kovar cap; 3, 4–elastic fiber-glass inserts (corrugated); 5–detonator; 6–hammerhead; 7–gas inlet of mass-spectrometer tube; 8–Kovar ring; 9–stainless steel disk; 10–annular vacuum seal; 11–body of rocket; 12–Kovar ring; 13–mass-spectrometer tube; 14–annular vacuum seal; 15–stainless steel bellows; 16–foam-rubber.

now consisted no longer of a three-stage tube, but of a four-stage glass 5–7-cycle tube (Figure 56). Moreover, the method used to open the inlet tube of the apparatus was an incomparable improvement on that previously used /113/; this clearly played a decisive role in improving the reliability of the experiment. The system used is shown in Figure 57. The nose tip of the rocket, which covers the mass-spectrometer tube during the rocket flight through the dense layers of the atmosphere, is jettisoned at the right moment by special springs. At the same time, the opening mechanism breaks the inlet tube and is discarded along with the now no longer necessary protective nose tip. The wide inlet of the mass-spectrometer tube is now right at the front of the rocket, and there are no surfaces which can emit gas in its field of vision.

The change described above represented a considerable improvement in the experimental techniques used in investigating the upper atmosphere. Thanks to this, the results obtained during the 1956 ascent were considerably more reliable than those obtained during the previous flight (in 1953).

As in the previous experiment (Aerobee NRL-13), the main attention in the 1956 work was focussed on the gravitational separation of gases. The argon-nitrogen ratio was again taken as an index of the degree of separation: if separation was present, this ratio should decrease with

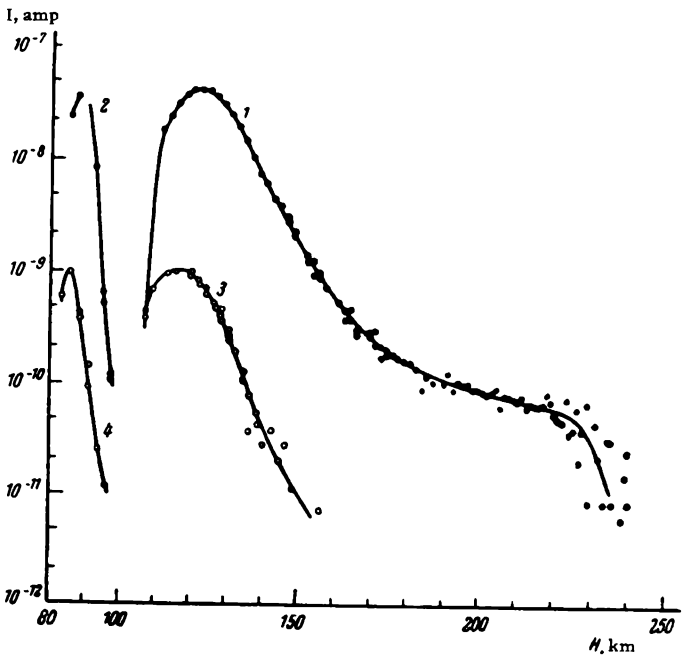

FIGURE 58. The ion currents of molecular nitrogen and argon as functions of height

1 and 2—ascending and descending sections of the trajectory for nitrogen; 3 and 4—ascending and descending sections of the trajectory for argon.

height. The choice of these two elements was not made at random. They do not change state on collision with the hot filament of the ion source, nor on absorption of solar energy (nitrogen is practically undissociated at heights of 100–150 km). Moreover, as we have already mentioned (see Chapter IV) these two gases should give appreciable gravitational separation, since their molecular weights differ considerably. Figure 58 shows the ion currents for A and N_2 as functions of the rocket's height. Most of the data were obtained during the ascent of the rocket from 105–241 km. Hardly any data are available from the descent, because, as was later stated /112/, during the rocket's return to Earth the inlet of the mass-spectrometer tube was in a region of "molecular shadow". The sudden appearance of data between the heights of 98 and 83 km is presumable due to the fact that the rocket here turned nose downwards, so that the gas molecules could again freely enter the mass-spectrometer tube.

The data of Figure 58 were used to calculate the ratio A/N_2 for each kilometer in the interval 110–150 km. After introducing the appropriate dynamic and calibration corrections, the separation coefficient $r = A/N_2 : A_0/N_{2_0}$ could be determined, where A_0/N_{2_0} is the value of the ratio at ground level. The final results are plotted in Figure 59. The three continuous lines in this figure represent theoretical calculations of the

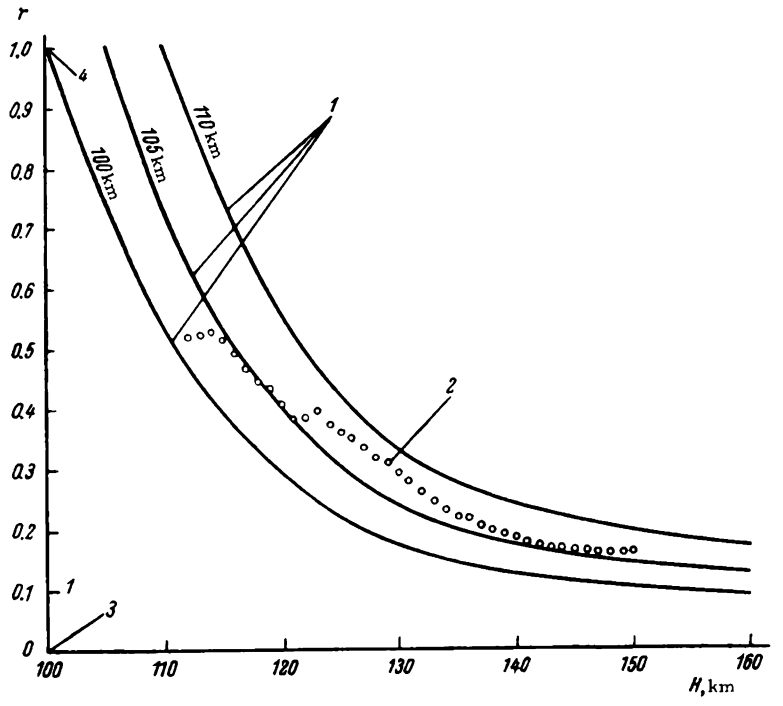

FIGURE 59. The gravitational separation of the gases nitrogen and argon

1–theoretical curves; 2–experimental points; 3–point corresponding to complete separation; 4–point corresponding to complete mixing.

course of the gravitational separation of nitrogen and argon with height, on the assumption that the lower limit of gravitational separation is 100, 105 or 110 km. For example, we see from the bottom curve that if gravitational separation began at a height of 100 km, we should expect to find a separation coefficient $r = 0.5$ at a height of 111-112 km, while the top curve shows that if gravitational separation began at 110 km we might expect to find the same value of r at 122 km, etc. The experimental points all lay quite close to the curve calculated on the assumption that the gravitational separation began at a height of 105 km. This led the authors to conclude that they really had found gravitational separation of gases in the Earth's gravitational field, starting at a height of 105 km. This was the first and most important result of the experiment of 20 February 1956. The second result was the detection of other atmospheric gases. Unlike the flight of the Aerobee NRL-13, the flight of the Aerobee-Hi NRL-48 only detected gases which we can expect to be present in the atmosphere. Apart from argon (40) and nitrogen (28), the following gases were found: CO_2, (44), O_2 (32), NO (30), H_2O (18), O (16) and N (14).

However, it was not yet possible to give a well-defined quantitative analysis of the gaseous composition of the atmosphere based on the values of the ion currents measured in the mass spectrometer.

The situation is complicated by the fact that gases containing unstable elements can undergo two different processes in the analyzer: recombination on the glass walls of the inlet tube and dissociation on the hot filament of the ion source or by bombardment of the gas molecules by thermal electrons. These two processes alter the original concentration of the gases and introduce a considerable element of uncertainty into the quantitative results. The authors therefore limited themselves to qualitative conclusions, which we reproduce below.

1) **Atomic oxygen (O).** At altitudes from 110—125 km, the O/O_2 ratio was equal to that determined in the laboratory for ground-level air (absence of atomic oxygen in the atmosphere). A sharp increase in the concentration of atomic oxygen was observed at height above 204 km.

2) **Nitric oxide (NO).** This gas, like atomic oxygen, may be formed inside the mass spectrometer. Up to a height of 120 km, the amount of NO found was equal to that for ground-level air (absent). Above this height, the NO concentration increased rapidly, but the authors did not draw any conclusions about its abundance in the atmosphere.

3) **Water (H_2O) and carbon dioxide (CO_2).** The CO_2 concentration found during the flight was about half that obtained on calibration with ground-level air, and the water concentration was about 1/10. However, since these components (in particular water) varied widely, it is difficult to draw a more definite conclusion.

4) **Atomic nitrogen (N).** The N/N_2 ratio determined during the flight varied little from that found with ground-level air; it may thus be said that the flight gave no information about the presence of atomic nitrogen in the atmosphere.

5) The mean molecular weight of the gases in the spectrometer remained practically constant up to an altitude of 170 km.

The authors concluded that the overall error involved in the measurement of the gravitational separation did not exceed 25%; the error was less at low altitudes than at high altitudes.

Ascents of the rockets Aerobee-Hi NRL-3.18F and Aerobee-Hi NRL-3.19F in the Arctic

The next step in the American investigation of the neutral composition of the atmosphere using radio-frequency mass spectrometers took place about one and a half years after the ascent of the Aerobee-Hi NRL-48, when two rockets were launched from Churchill in relatively quick succession: the Aerobee-Hi IGYNN-3.18F (21 February 1958) and the Aerobee-Hi IGYNN-3. 19F (23 March 1958). The first of these was launched during the polar night, at 2002 hours (Central Standard Time), and penetrated into the region of the aurora, reaching an altitude of 225 km. The second was launched during the polar day, at 1207 hours, and reached an altitude of 203 km. Both rockets were fitted with exactly the same equipment as the Aerobee-Hi NRL-48, which we have already described.

The main result of both these flights was the observation of the level of gravitational separation of gases both during the polar day and during the polar night /114/. This is shown graphically in Figure 60, which also includes the results obtained during the flight of the Aerobee-Hi NRL-48. As

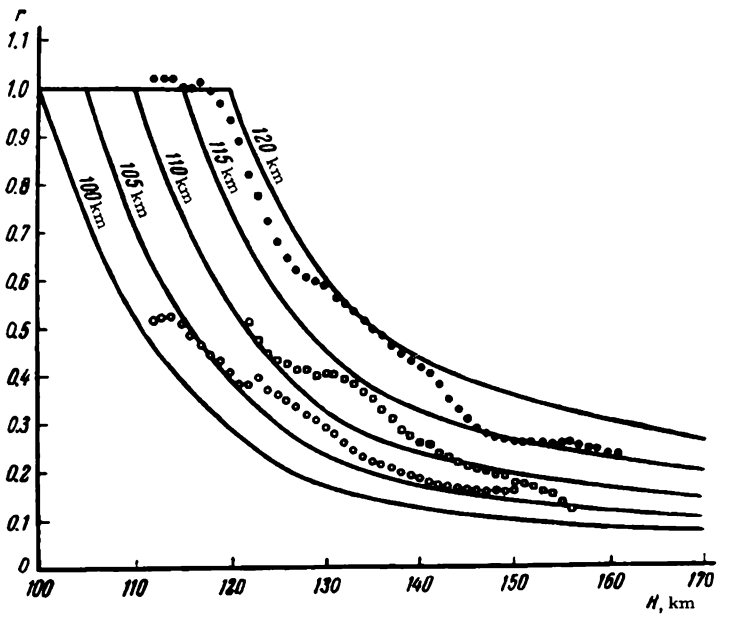

FIGURE 60. Composite graph of three experiments to determine the level of gravitational separation of the atmospheric gases in the Arctic

○,□,● –results of three different experiments.

can be seen from the figure, a lower limit for the gravitational separation was found in each experiment, this lower limit occurring at a different altitude each time. The highest altitude (115-120 km) was found during the day (23 March 1958). It may be concluded from the results of these three experiments that the lower limit of gravitational separation fluctuates between 105 and 120 km above sea level.

In all these experiments it was found that the ion-current ratio O/O_2 varied very little, at least up to an altitude of 150 km. This indicates that the concentration of molecular oxygen remains high up to this height, although considerable dissociation of oxygen occurs from about 100 km.

The discrepancy between the results of the mass-spectrometric investigation and the theoretical conclusions about the photochemical equilibrium of the atmosphere in the layer from 100 to 150–200 km is easily explained by the fact that it is possible for the oxygen atoms to recombine to form molecules on entering the mass spectrometer.

On the basis of further processing of the data obtained from the flights of these three rockets, Townsend, in a recent publication /134/, drew a surprising conclusion about the observed ratio of the ion currents of atomic and molecular oxygen recorded by the mass spectrometer.

He suggested that if the above explanation of the difference between the experimental and theoretical values be true, then the value of the O/O_2 ion-current ratio should depend strongly on the angle of incidence of the mass-spectrometer tube; in other words, this ratio should be a function of the angle between the velocity vector of the rocket and the axis of the mass-spectrometer tube. In fact, if the axis of the tube coincides with the velocity vector (angle of incidence = 0) the atmospheric particles should be able to pass directly to the collector of the tube, so that the observed value of the ratio O/O_2 should give a true picture of the state of the oxygen in the atmosphere. If the axis of the tube is at an angle to the velocity vector, the O/O_2 ratio should be shifted more and more towards O_2 (i. e., should decrease) as the angle in question increases, since under these conditions an increasing number of atmospheric particles can only reach the collector of the mass spectrometer after several collisions with the glass walls of the tube, each collision increasing the probability of recombination of the oxygen atoms. Examining the experimental material from this point of view, Townsend failed to find the expected relationship: on the contrary, the O/O_2 ratio behaved in the same way for all three arctic rockets, although the angle of incidence varied with height in a completely different way for each rocket. This is shown in Figure 61.

It would thus appear from this that the experimental data concerning the ratio of atomic oxygen to molecular oxygen to give a true picture of the situation in the atmosphere, i. e., that the oxygen atoms do not recombine on the walls of the tube (?).

However, as V. G. Istomin /144/ remarked, the situation is much more complicated than this. When the mass spectrometer is working normally, there are always two opposed streams of gaseous particles in the analyzer tube: one from the atmosphere into the tube and the other (of "spent" particles) out of the tube. On passing through the ionization space

of the apparatus, the particles of both streams are ionized with equal probabilities and proceed to the collector under the influence of the electric field.

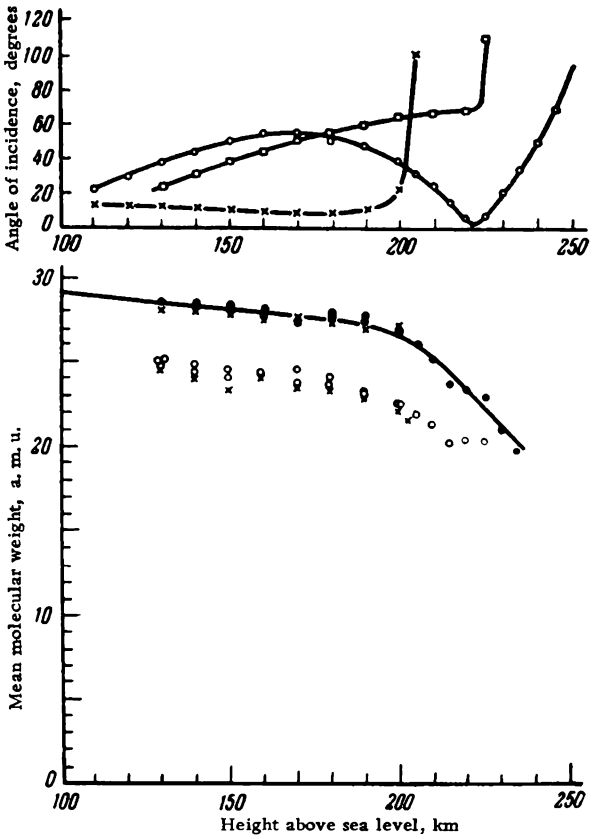

FIGURE 61. Variation of mean molecular weight with height

O–night; x–day; ●■x –measured values; OCX –minimum values.

When the mass spectrometer is operating in regions where atomic oxygen is present, the recombination of the oxygen atoms in the analyzer tube will lead to a difference in composition between the incoming and the outgoing stream of gas: the outgoing stream will always be richer in molecular oxygen. The recording of these "artificial" molecules by the apparatus can lead to a false picture of the composition of the layer of the atmosphere in question. Since no direct experimental investigation of the behavior of atomic oxygen in the mass-spectrometer tube has yet been made, it is at present difficult to estimate the proportion of molecules in the stream of "spent" particles formed by recombination. It seems likely

that this proportion is quite large and, of course, independent of the orientation of the mass spectrometer. The quantitative conclusions drawn by Townsend (Figure 61) about the presence of molecular oxygen in the atmosphere at high altitudes must therefore be treated with caution, although the qualitative picture of this increase sketched by Nicolet and Mang /135/ apparently corresponds fairly well to the real state of affairs*. In the light of the above, the conclusion as to the relatively high mean molecular weight in the layer of the atmosphere from 100–200 km should also be treated with caution.

The above-mentioned rocket flights represent all that has been done up to the present outside the Soviet Union in investigating the neutral composition of the atmosphere at high altitudes.

4. Investigations of the neutral composition of the atmosphere carried out in the Soviet Union

A Bennett-type mass spectrometer was sent up to about 200 km in the middle latitudes of the USSR in the summer of 1959, for investigating the neutral composition of the atmosphere.

This mass spectrometer, which was made in the GSKB AN SSSR**/145/ on the basis of the existing mass spectrometer designed by V. G. Istomin (1956), was intended for investigating both the neutral and the ionic composition of the atmosphere***. The new apparatus, which is shown in Figure 62, has the advantage that it can be used to analyze the light gases hydrogen and helium, the problem of whose presence in the upper atmosphere has provoked and continues to provoke considerable controversy. In fact, the question as to whether the light gases play an important role in the formation of the upper atmosphere, and if so at what height, is of great significance not only for geophysics but also for astrophysics.

In contrast to the American work described above, in these experiments the radio-frequency mass spectrometer was mounted in an automatic container, which is shown in Figure 63. This container very closely resembles the one described in the previous chapter. The main difference is that the open compartment is now replaced by a hermetically sealed compartment containing the telemetering system, an oscillograph which duplicates the telemeter record, and the radio-frequency mass spectrometer. The transmitting antennae are outside the compartment.

The analyzer tube of the radio-frequency mass spectrometer passes through the side wall of the compartment, thus communicating with the atmosphere. The tube is fitted with a special flange to ensure a hermetic seal at the point where it passes through the wall of the compartment. In

* According to Nicolet and Mang, the distribution of atomic and molecular oxygen in the atmosphere between 100 and 200 km is not determined by the photochemical equilibrium. The oxygen in this layer is subject to diffusion, which causes the oxygen molecules to rise, during which process they are not ionized immediately by the solar radiation because of its low intensity.

** [Gosudarstvennoe spetsial'noe konstruktorskoe byuro Akademii Nauk SSSR—State Special Design Bureau of the Academy of Sciences of the USSR.]

*** The investigation of the ionic composition is described in Section 7.

order to eliminate the undesirable influence of gas emitted from the container's surface, the tube is mounted in a wide depression, so that the surfaces of the container proper are as far as possible out of the field of view of the apparatus*.

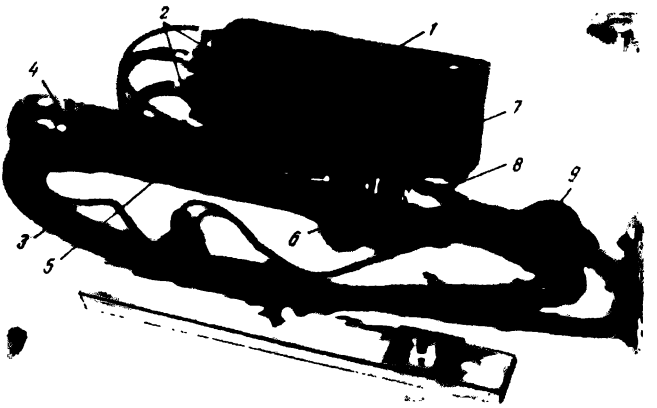

FIGURE 62. The radio-frequency mass spectrometer used in the Soviet investigations for the analysis of the ionic and neutral composition of the atmosphere

1—electronics of mass spectrometer; 2—plug connectors; 3—connecting cables; 4—preamplifier; 5—metal analyzer tube; 6—flange for fixing tube to rocket; 7—double flange for connecting ion source; 8—ion source; 9—glass bulb with getter, which is broken at start of operation of mass spectrometer.

During the upward flight of the rocket the container containing the mass spectrometer is ejected by means of a mortar and describes its own trajectory. At a given height the mass-spectrometer tube is opened and the analysis of the surrounding gas begins.

The work of determining the neutral gaseous composition of the atmosphere by the method described above was carried out by A. A. Pokhunkov /115/ and led to the following results.

The mass spectrometer recorded ten sorts of ions produced in the ion source of the apparatus, which were identified with the gases H, H_2, OH, H_2O, N, O, N_2, O_2, A and CO_2. The character of the peaks in the spectrograms allows the above-mentioned gases to be divided into two main groups: water and its derivatives (H_2O, OH, H, H_2), which form part of the stray gases from the container itself and the rocket, and the atmospheric gases (O, N, O_2, N_2, A, CO_2).

This clear-cut division into two groups could be confirmed as a result of the container's rotation, produced by the firing from the mortar. Thanks to this rotation, the orientation of the axis of the mass-spectrometer tube with respect to the velocity vector of the container varied, and with it

* Under experimental conditions the inlet of the analyzer tube projects below the container.

varied the overall pressure in the tube: this pressure was maximum when the angle between the axis of the tube and the velocity vector was minimum, and was minimum when this angle was greater than 90°, i. e., when the

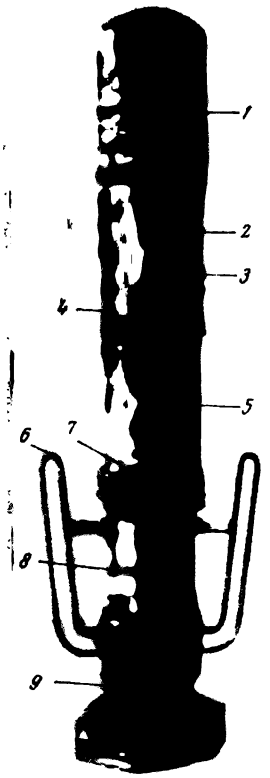

FIGURE 63. Automatic container with radio-frequency mass spectrometer

1–parachute compartment (with braking system removed); 2–wide depression containing the inlet of the mass-spectrometer tube; 3–hermetically sealed compartment containing the electronics of the mass spectrometer; 4–manometer window; 5–instrument compartment; 6–transmitting antennae; 7–window admitting light to cameras; 8–power-supply compartment; 9–buffer cone.

inlet of the mass-spectrometer tube was in the "molecular shadow" cast by the container. As a result of this, the heights of the peaks corresponding to the atmospheric gases fluctuated considerably with a period equal to the container's period of rotation (Figure 64). The intensities of the peaks due to the stray gases naturally did not show this fluctuation, since the pressure due to the cloud of gas emitted by the container did not depend on the orientation of the latter (Figure 65).

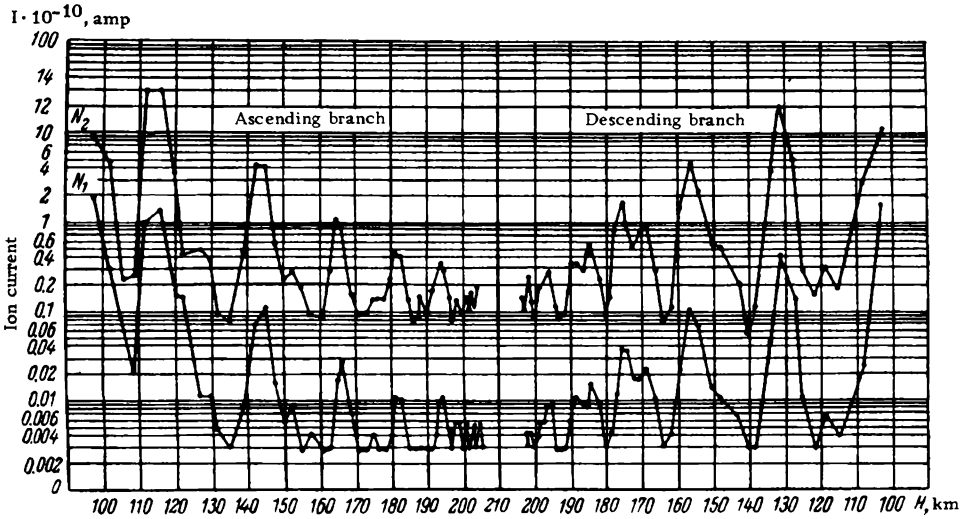

FIGURE 64. Variation of the amplitude (pulse height) of the ion current for molecular and atomic nitrogen, due to the rotation of the container

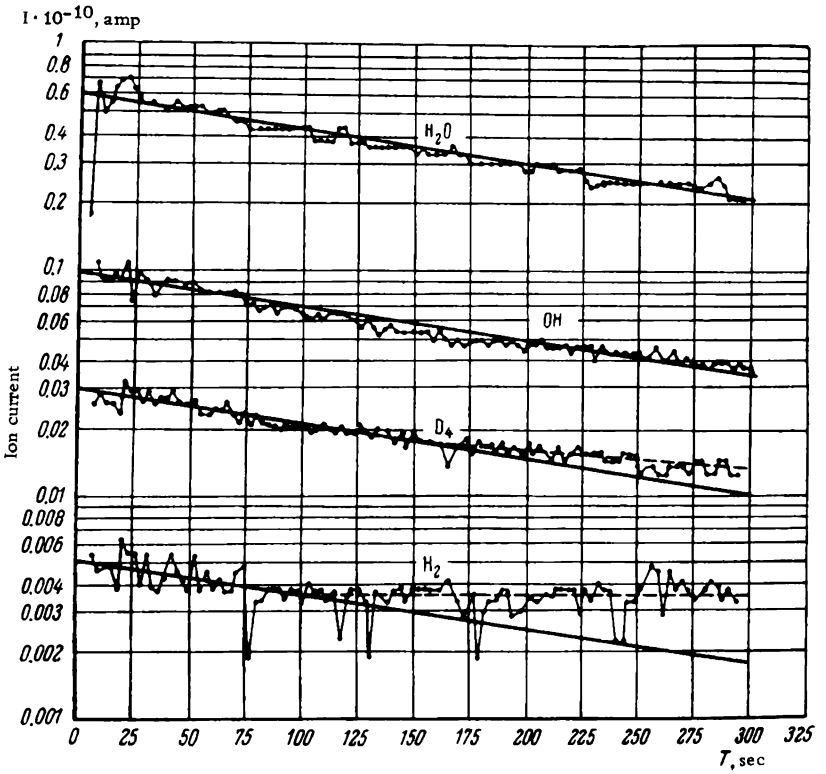

FIGURE 65. Aperiodic fluctuation of the ion currents for the gases of the water group

It can be seen by examining Figure 65 that the concentration of the gases of the water group shows a gradual monotonic decrease with time during the whole flight; this provides a further confirmation that these gases are produced by desorption from the container. If we further assume that this desorption can be represented, to a good degree of approximation, by an exponential function $I = I_0 l^{-\frac{t}{\tau}}$, we find a good agreement between theory and experiment in the case of water (I_0 = ionic current at $t = 0$; we see from Figure 65 that this is equal to $6 \cdot 10^{11}$ amp for water. The time constant is in this case equal to 316 sec).

A certain discrepancy between the experimental and theoretical curves is found only in the case of H and H_2. In the case of molecular hydrogen, this discrepancy can be explained as being due either to the presence of hydrogen of atmospheric origin, or, which seems to us more likely, to the evolution of hydrogen from the internal surfaces of the analyzer tube*. Expressed in terms of ion current, this excess of hydrogen is estimated as $3 \cdot 10^{-13} - 2 \cdot 10^{-13}$ amps. This led Pokhunkov /115/ to conclude that the amount of neutral hydrogen in the atmosphere at altitudes between about 100 and 200 km could in any case not exceed 10^8 particles per cm^3, an amount which lies near the limits of sensitivity of the apparatus.

The rotation of the container, while facilitating the division of the gases into atmospheric and stray, also gave rise to difficulties in the processing of the spectrograms of the atmospheric gases. Since this processing was carried out on data which could not be corrected "for orientation", the only points chosen for further calculations were those lying at the maxima of the original curves (see Figure 64). This unfortunately greatly reduced the amount of useful information.

In the second stage of the processing of the data, the selected points from the original ion-current curves for any two gases were compared one with another. For example, analysis of the ratios of the peak heights for N and N_2 showed that atomic nitrogen does not occur in appreciable amounts between 100 and 200 km (Figure 66).

The same procedure for atomic and molecular oxygen only gives a qualitative picture of the distribution of this element since, as we have seen in the previous section, a considerable amount of atomic oxygen may recombine to form molecular oxygen between entering and leaving the analyzer of the mass spectrometer. Despite this, however, the general picture of the distribution of atomic oxygen is fairly clear: the increase of atomic oxygen with respect to molecular oxygen begins at the lowest altitudes at which measurements were made (about 100 km), and continues right through the investigated range (up to about 200 km).

The analysis of the variation of the ratio of the two inert gases (A/N_2) with height is of considerable interest for determining the gravitational separation of gases. The experimental data processed by A. A. Pokhunov showed that gravitational separation began at an altitude of about 100 km, but the limited number of experimental points did not allow the author to draw any quantitative conclusions. Helium and hydrogen

* Before opening, this tube was filled with a mixture of H_2, He, Ne and A for the purposes of calibration before and during the flight.

were not found in appreciable amounts ($>10^8$ atoms/cm^3) in these experiments.

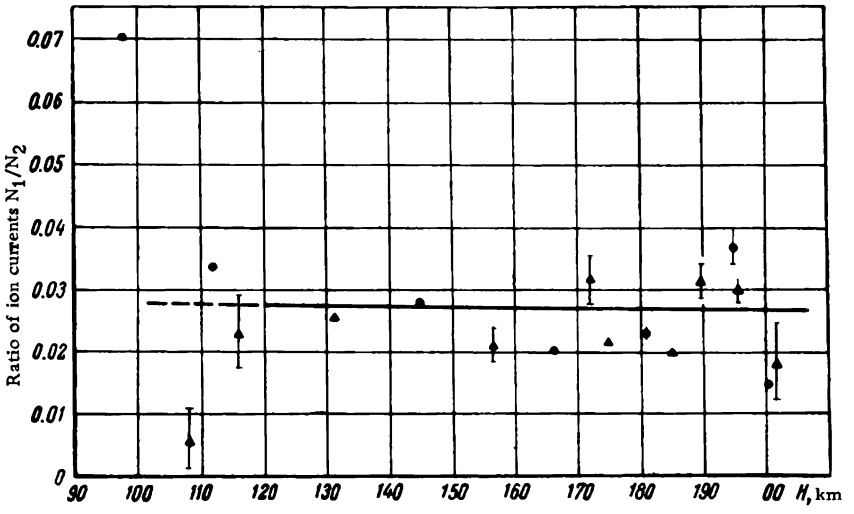

FIGURE 66. Ratio of ion currents for atomic and molecular nitrogen as a function of height

●–ascent; ▲–descent.

5. Discussion of results

The first experimental investigation of the gaseous composition of the atmosphere, carried out on 12 February 1953, had the nature of a trial run. It enabled the apparatus to be tested and the experimental method to be refined. As a first experiment, it had a number of serious faults; but it played a great role in preparing the way for further similar investigations. In this respect, the work of Townsend and his collaborators was of indisputable significance.

On the other hand, the geophysical conclusions drawn from the flight of the Aerobee NRL-13 are in our opinion not sufficiently reliable. The imperfections of the experimental method also affected the results: the large amounts of various gases which clearly did not come from the atmosphere itself and which were recorded by the mass spectrometer showed that the conditions at the input of the mass spectrometer could be considerably improved. The authors themselves acknowledged this fact, and suggested a number of reasons for the contamination of the atmospheric gas. However, they did not even consider the most important reason for doubting the accuracy of the experimental results published in /111/: the inexcusable fact that the inlet of the mass-spectrometer tube was inside the nose compartment of the rocket. Despite the fact that the flow rate through the apertures connecting this compartment with the outer atmosphere was sufficiently high (about 900 liters per sec, and the total volume of the nose

compartment was 9 liters), this did not guarantee that the gas reaching the measuring equipment was a representative sample of the surrounding atmosphere. At high altitudes, where the mean free path of the molecules is large, the molecules rarely collide with one another in the small volume surrounding the inlet of the mass spectrometer. Consequently, most molecules reaching the mass spectrometer will have come straight from the inner wall of the nose compartment. These repeated collisions with the wall of the nose cone may well cause the particles of the gas to change state (by recombining for example) before entering the mass spectrometer. We must also consider the large number of stray molecules emitted by the walls of the protective cone, which under the present conditions (absence of collisions in the compartment) can pass straight into the mass spectrometer. These effects are amplified many-fold if, as stated by the authors and as confirmed by the intense ion-current peaks in groups II and III, the nose of the rocket is strongly heated during the ascent. Heated metal enters actively into all sorts of reactions with the atmosphere and also emits enormous quantities of occluded gases, and may thus completely distort the true picture of the atmosphere. Just as undesirable as the situation of the inlet of the mass spectrometer inside the shell of the rocket is the presence of mechanisms lubricated with oil near this inlet (the opening mechanism). Nor is it very suitable that the mass spectrometer is situated in a massive rocket which itself emits a large amount of stray gases and which in certain positions during its flight may create a wide region of molecular shadow round the mass spectrometer; this happened, for example, during the flight of the Aerobee-Hi NRL-48 (no data during the descent).

These shortcomings of the experiment prevented the authors from drawing practically any conclusions about the presence of any given gas (although they did put forward a number of hypotheses). It is strange that no gravitational separation between argon and nitrogen was observed right up to the maximum altitude reached (137 km).

The results obtained with the Aerobee NRL-13 were in contradiction with those of previous investigations (see Chapters III and IV), which had indicated gravitational separation somewhere around 100 km. As we have seen, later measurements by the same authors, carried out, it is true, in the Arctic, also indicated separation at these altitudes. Nevertheless, Townsend and others concluded (1959) that the results of the first successful flight did represent the real state of the atmosphere above New Mexico on 12 February 1953. The authors explained the contradiction between the data obtained by the flight of the Aerobee NRL-13 and by that of the Aerobee-Hi NRL-48 as being due to the difference in latitude between New Mexico and Fort Churchill.

In our opinion, it is hardly possible to maintain that the experimental results obtained with the Aerobee NRL-13 were accurate. It is more reasonable to assume that the cap over the inlet of the mass spectrometer hindered the investigation of the gravitational separation of nitrogen and argon, by acting as an unusual kind of "trap", which enriched the gas round the inlet in argon. The surrounding atmosphere, consisting of a mixture of different gases, reached the inlet of the mass spectrometer through the slits in the cap. If the mean free path of the molecules were small, this

would have no effect on the composition of the gas reaching the analyzer. The picture alters sharply when the mean free path equals the distance between the inner walls of the protective cone*, i. e., when the molecules entering the nose compartment through the slits can only leave it after repeated collisions with the walls. In this case, the "fast" nitrogen will leave the nose compartment in greater amounts than the "slow" heavy argon. This will give a false conclusion as to the gravitational separation of these gases.

The other three experiments with Aerobee-Hi rockets in the Arctic were carried out considerably better. The jettisoning of the nose cone represents a great improvement in the experimental method, making the results concerning the detection of gravitational separation much more reliable. All three experiments indicated the presence of gravitational separation, which, in our opinion, would also have been discovered at the more southern latitudes if the improved experimental method used for the arctic experiments had been used there too.

Confirmation of this is provided by the similar experiments by Soviet investigators /115/, carried out in the medium latitudes of the European territories of the Soviet Union, in which the beginning of gravitational separation between these gases was observed at altitudes between 100 and 115 km.

If we consider the results of the rocket experiments involving the taking of samples (Chapters III and IV), which also indicated the presence of gravitational separation at both medium and low latitudes, it seems perfectly justified to conclude that gravitational separation of the gases nitrogen and argon begins everywhere at altitudes of about 100–120 km.

The fact that the height at which this separation begins is variable, as was shown by the experiments with the Aerobee-Hi rockets, is of great interest. This fluctuation may be due to the variations in temperature and density which are characteristic of the upper atmosphere. It is also possible that this fluctuation is due to variations in the physical conditions of the lower atmosphere. The shortage of experimental data makes it difficult to reach a firm conclusion on this point at present.

The investigation concerning the presence of the light gases in the upper atmosphere, carried out by the Soviet investigators /115/, is of exceptional interest. The absence of these gases in amounts which could be recorded by the measuring equipment (10^8 particles per cm^3) indicates that the atmosphere does not contain detectable amounts of hydrogen or helium at the altitudes investigated (up to 200 km).

Supply of gas to the Earth's atmosphere may come either from the Earth itself or from outer space. The latter (corpuscular radiation from the Sun) cannot be responsible for considerable concentrations of the light gases at heights above 200 km, as these gases would find it difficult to maintain a stable existence in the "hot" (2000–3000°K) upper atmosphere. Supply of hydrogen and helium from the Earth cannot give rise to greater absolute concentrations of these gases above 200 km than are found below this height, since there are no additional sources which can "generate" these gases

* This is so at altitudes above 110 km, i. e., along nearly all the path covered by the mass spectrometer during its operation.

above this altitude*. It may therefore be concluded, on the basis of the investigation of the concentration of hydrogen atoms and molecules at altitudes around 200 km, that even if the concentration of hydrogen decreases very slowly (because of the high temperatures), hydrogen cannot predominate in the atmosphere at least up to altitudes where the overall concentration of molecules is of the order of 10^8 per cm^3. In other words, an appreciable hydrogen atmosphere cannot be expected, at the very lowest, below altitudes of 400–500 km.

FIGURE 67. The analyzer tube of the three-stage mass spectrometer for detecting ions

Additional evidence may be obtained from the results of the investigation of the ionosphere up to altitudes of 1000 km (see Chapter VI), where no signs of the presence of any hydrogen-containing ions (in the first place hydroxyl) in the atmosphere were found**; it may thus be concluded that hydrogen does not form an appreciable part of the atmosphere right up to 1000 km. It follows that in the lower atmosphere where the direct investigation of hydrogen was carried out (100–200 km), its concentration must be considerably less than the limits of sensitivity of the equipment used in the investigation /115/, i. e., considerably less than 10^8 particles per cm^3.

6. Investigations of the ionic composition of the atmosphere carried out in the USA

Alongside the investigation of the neutral composition of the atmosphere, in 1954 the USA began to investigate the ionic composition of the ionosphere. For this purpose they normally used the same Bennett-type radio-frequency mass spectrometer used for analyzing the neutral gas.

The "ionic" radio-frequency mass spectrometer is somewhat simpler to use, and the results obtained give an appreciably better picture of the composition of the ionosphere than that of the composition of the neutral gas obtained with the "neutral" version of the mass spectrometer. The absence of an ion source with its hot filament

* For helium, this conclusion is true at all altitudes. This inert gas, which does not react with the other components of the atmosphere, can diffuse freely through the atmosphere into outer space. The situation is different with hydrogen. It appears that at 90–100 km a photochemical reaction takes place leading to the dissociation of water vapor coming from the lower layers of the atmosphere into hydrogen and oxygen. As a result of this, the concentration of hydrogen in the atmosphere may increase at altitudes of 90–110 km. There are no other sources of "terrestrial" hydrogen in the atmosphere above this altitude.

** The mass spectrometer used in the satellite could not measure the light masses of the hydrogen and helium ions directly.

in the "ionic" apparatus means that the different molecules of the atmosphere under investigation, in particular oxygen molecules, do not dissociate in the apparatus. The absence of an ion source also makes it possible to give the analyzer tube a wide inlet, and the inwardly directed field of the apparatus prevents ions which reach the input from colliding with the walls. The electric field of the analyzer guides the ions into a trajectory which is strictly parallel to its axis; since the velocity given to the ions by this field is about two orders of magnitude greater than that due to the thermal motion of the ions, the latter does not affect the trajectory of the ions appreciably. The absence of a special ionization region in the apparatus means that the counter-current of "spent" neutral gas particles* is not recorded by the mass spectrometer at all, and the ionic composition of the sample of the ionosphere is not altered inside the apparatus. Although the "ion" version thus lacks these two disadvantages of the neutral analyzer, it does have its serious drawbacks, the most important of which is a result of the electrostatic charge on the rocket which can displace the ion-current peaks by several atomic mass units along the voltage scale. Knowing the rocket's charge, one can of course correct for this, but this charge is usually only known approximately. Moreover, it is impossible to determine the rocket's charge beforehand**, which may lead to an incorrect choice of the retarding voltage of the apparatus so that the apparatus is either "shut off", or "opened" so much that a large number of unnecessary harmonic peaks are obtained, which make the identification of the "real" peaks much more difficult. This was in fact the case in the first ascent of an ion mass spectrometer, in the "Viking-10" rocket from White Sands, 7 May 1954 /116/. During the ascent, the rocket unexpectedly developed a large negative charge, which together with the large evolution of gas from the rocket made it impossible to interpret the data obtained.

Ascents of the rockets Aerobee-23 and Aerobee-24, White Sands

The rocket Aerobee-23 was launched from the White Sands proving ground on 8 July 1955 at 0139 hours (Mountain Standard Time, meridian 105°) /117/. The rocket reached an altitude of 115 km and reached the nocturnal sporadic E layer. Two mass spectrometers were mounted in the rocket nose for determining both positive and negative ions. The construction of the two mass spectrometers was identical, and is shown in Figure 67. The grid voltages of the apparatus for determining the negative ions were opposite in sign to those of the apparatus for the positive ions. Unlike the "neutral" models, the ionic mass spectrometers had their inlet tubes open right from the start of the flight, so that the opening mechanism could be dispensed with. The apparatus was switched on at the start of the flight, and began to work of its own accord as soon as the pressure in the analyzer fell to the desired level (in the case of the Aerobee-23 this occurred at an altitude of 93 km). In order to protect the apparatus from the high velocity pressures which the rocket underwent during its ascent through the dense

* See p. 127.

** A recent paper by Johnson /133/ describes a device for determining the mass numbers absolutely without knowledge of the rocket's charge, but this entails a special periodic variation of the retarding voltage of the mass spectrometer.

lower atmosphere, the mass spectrometer tube was placed behind a nose cone, which was automatically jettisoned at a given moment, freeing the tube for operation. The data obtained during the flight indicated the presence of only one positive ion, of mass number 28(N_2^+), in the atmosphere (at night-time, 8 July 1955). The variation of the ion current of this peak with height is shown in Figure 68. The authors explained the regular

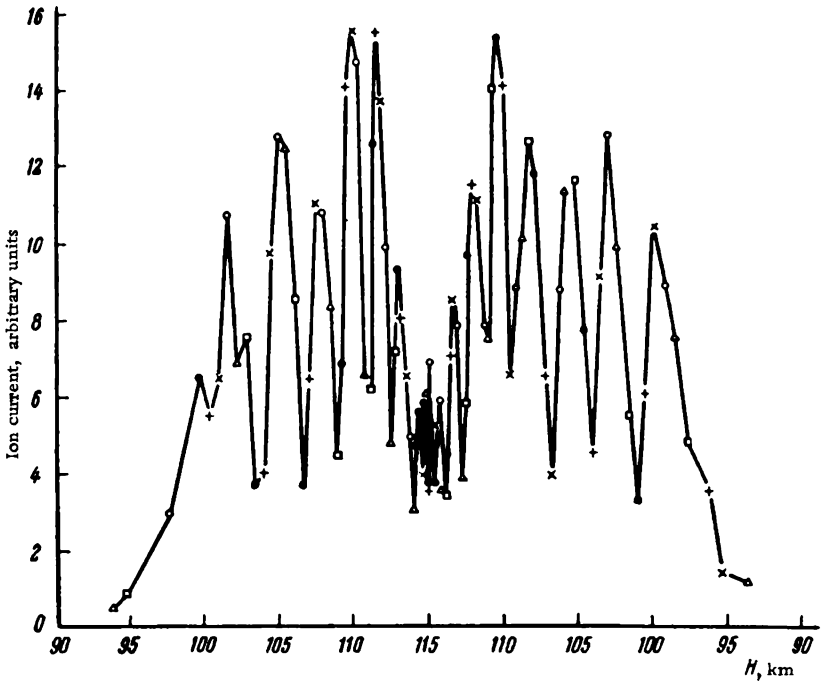

FIGURE 68. The ion current for N_2^+ as a function of height

variation of peak height with altitude as being due to the rotation (precession) of the rocket during its flight.

During the same flight a small peak of negative ion current was also recorded, corresponding to mass 46 (NO_2^-). This peak was observed at altitudes above 112 km during the ascent and down to 110 km during the descent, i. e., right at the peak of the trajectory*.

The rocket Aerobee-24 /118/ was fitted with the same equipment as the Aerobee-23. It was also launched from White Sands, on 29 November 1955 at 1016 hours, Mountain Standard Time. This rocket reached an altitude of 131 km; the recording of the ion spectra started at 113 km during the ascent and continued until 93 km during the descent. During this daylight flight, only negative ions were recorded, with masses of 46 (NO_2^-), 32 (O_2^-), 22 (?) and 16 (O^-). Among these ions, NO_2^- was much the most abundant, its ion current making up 97 % of the total. The authors could not explain the absence of positive ions in the atmosphere; a (telemetric) check of the operation of the mass spectrometer for positive ions indicated that it was working normally.

* It is quite possible that the NO_2^- was formed by the dissociation of the nitric acid used as oxidant in the Aerobee rocket.

Ascent of the rocket Aerobee-Hi NRL-48 in the Arctic

We have already mentioned the ascent of the Aerobee-Hi NRL-48 in the section on the investigation of the neutral composition of the atmosphere (p. 120). This rocket also carried two three-stage radio-frequency ion mass spectrometers /119/. The ion mass spectrometers were mounted so that their inlets projected through the side walls of the head of the rocket (Figure 69), the analyzers for the positive and negative ions pointing in diametrically opposite directions. The spectrometers covered the range

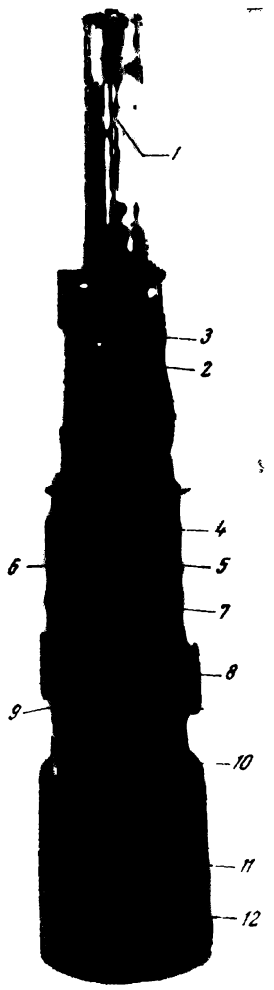

FIGURE 69. Equipment used in Arctic flights of the Aerobee-Hi rockets

1–mass spectrometer for neutral gas; 2–electronics of the mass spectrometer; 3–magnetic orienter; 4–batteries; 5–calibrator; 6–storage battery of disconnection switch; 7–switch box; 8–telemeter; 9–radio beacon; 10–switch for location receiver; 11–antenna of radio beacon; 12–ion mass spectrometer.

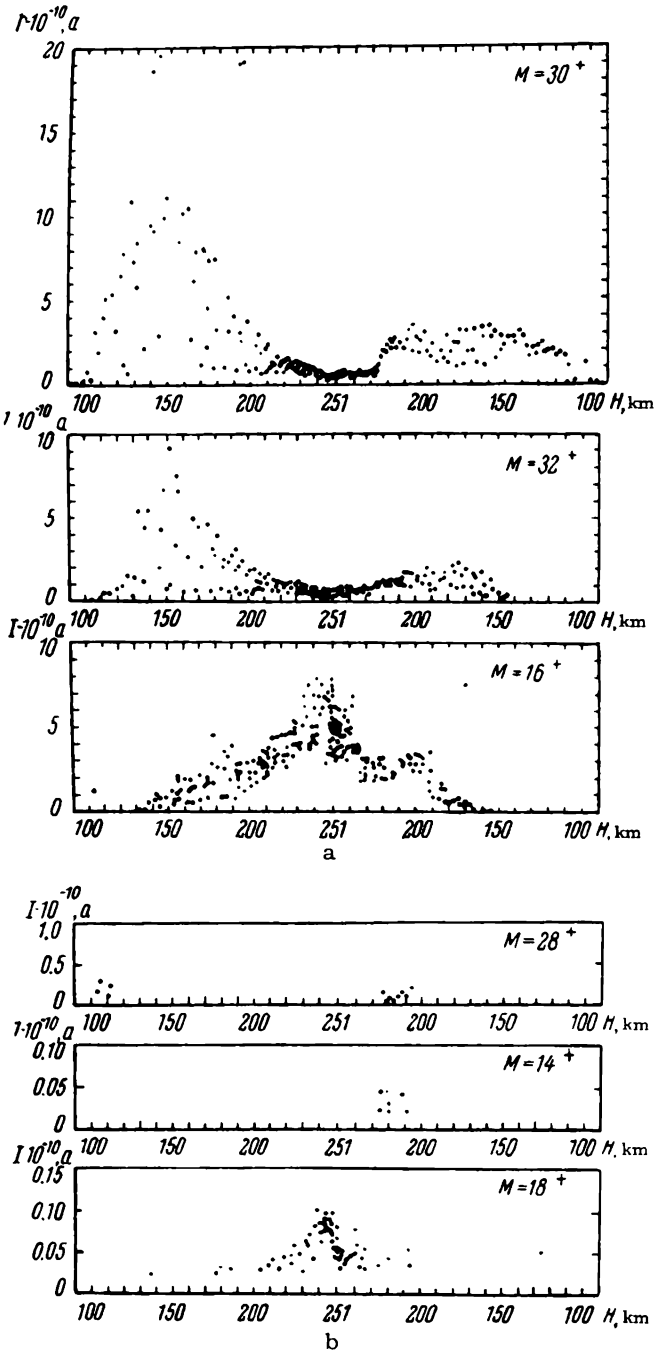

FIGURE 70. Ion currents as functions of height

a—main components of ionosphere; b—minor components of ionosphere.

from 6–53 atomic mass units. The spectra were obtained at night-time over a period of 375 sec, while the rocket was above the 90 km level. Six peaks were observed which definitely corresponded to positive ions of mass 14 (N), 16 (O), 18 (H_2O), 28 (N_2), 30 (NO) and 32 (O_2), and one peak which corresponded to negative ions of mass 46 (NO_2^-).

Figure 70a shows the variation of the concentration of the three main components of the ionosphere (NO^+, O_2^+ and O^+) with height between 100 and 250 km. As may be seen from the figure, the maximum concentrations of NO^+ and O_2^+ are found at about 150 km. The concentration of O^+ increases steadily from 120–130 km to the maximum height reached by the rocket, 251 km. The variation with height of the concentration of the minor components N_2^+, H_2O^+ and N^+ is shown in Figure 70b. The ion of mass 28 is recorded at a height of about 100 km and at 230 km (during the descent), and that of mass 14 at about 230 km. Appreciable quantities of water (?) ions of mass 18 were recorded from about 100 km. The concentration of this ion increases up to the maximum height reached by the rocket, when the corresponding current amounts to 1 % of the total current in the apparatus. The spread of the currents in Figure 70a and b is attributed by the authors /119/ to the variation in the orientation of the inlets of the mass spectrometers with respect to the velocity vector of the rocket (yawing).

Ascents of the rockets Aerobee-Hi NRL-3.18F and Aerobee-Hi NRL-3.19F, Arctic

These rockets, which we have already mentioned, carried the same equipment as the Aerobee-Hi NRL-48 (see p. 139). In both cases, during

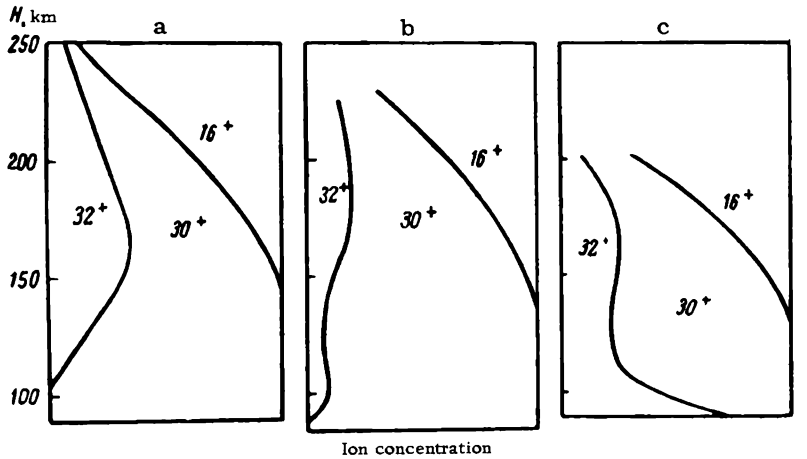

FIGURE 71. Composition of the ionosphere in the Arctic according to American data

a and b–night; c–day.

the night ascent (Aerobee-Hi NRL-3.18F, /120/) and during the day ascent (Aerobee-HI NRL-3. 19F, /120/), the same positive ions of mass 32, 30, 28, 18, 16 and 14 were recorded as during the ascent of the Aerobee-Hi NRL-48. Small amounts of the negative ion of mass 46 (NO_2^-) were also found. This ion was found every time an apparatus recording negative ions

was sent up. Figure 71 shows how the relative proportions of the principal positive ions in the ionosphere vary with height between 100 and 250 km. It is based on the data obtained during the flights of the three Aerobee-Hi rockets /120/, which gave concordant results.

7. Investigations of the ionic composition of the atmosphere carried out in the USSR

V. G. Istomin was the first to use a radio-frequency mass spectrometer for investigating the upper atmosphere in the Soviet Union, in 1957 /121, 122/. Previous to this, he and a group of co-workers put a great deal of work into the production of a model of this apparatus; they were greatly aided in this by a group from the Siberian branch of AN SSSR, led by N. A. Vorsin. This work was later published in a number of papers /123-125/, which gave the theoretical and experimental results obtained during the investigation. Istomin's apparatus was based on the same principle as Townsend's apparatus, but differed somewhat from the latter*. The main difference was the presence of "one layer" grids in the analyzer and ion source, used here for the first time in this kind of apparatus /126/. They should hinder the ion current as little as possible, and should be ideally flat; they are made of tungsten wire of diameter 12-20μ. It is a difficult matter to weave such grids, they hinder the ion current quite considerably, and moreover they are far from flat. A "one-way" grid is not a grid in the true sense of the word, but a parallel array of wires 18μ thick, stretched on a Kovar ring. The distance between the wires is 0.5 mm. It is stated /126/ that the resolution of a mass-spectrometer tube with one-way grids is somewhat greater than that of a similar tube using woven grids. A second improvement relates to the preliminary calibration: before the mass-spectrometer tube is finally sealed, it is filled with a mixture of the inert gases A + Ne and evacuated until the pressure is $3 \cdot 10^{-5}$ mm Hg. The tube filled with the inert-gas mixture was very convenient to work with; it could rapidly be adjusted at any time before the start, thus making all intermediate states of the calibration unnecessary.

The apparatus used by Istomin had the following parameters: a range of 6–50 atomic mass units, time taken to scan this range 1.7 sec, resolution in the neighborhood of mass number 28 given by $R = \frac{M}{\Delta M} = 28$, where ΔM is the width of a peak at its base, expressed in atomic mass units. The output resistance of the apparatus for direct current was 10^{10} ohms.

Ascent of geophysical rocket in the medium latitudes of the European territories of the Soviet Union, 9 September 1957

The radio-frequency mass spectrometer described above and illustrated in Figure 74, which was intended for the measurement of the mass spectra of positive ions, was mounted in the special container described above (see Figure 63). The inlet of the mass spectrometer passed through the side wall of the container in such a way that no gas-emitting (reflecting) surfaces

* For details see /130/.

were in its field of view. The container was carefully sealed and fitted with a radio-telemetering system which transmitted data to the receiving station on the ground. The container was sent up to an altitude of 206 km by rocket and returned safely to the ground by parachute. The flight took place in the evening of 9 September 1957, in the middle latitudes of the European territories of the USSR /121/. The rocket left the Earth's shadow soon after the launching, so that the measurements were carried out in a region which was directly lit by the Sun's rays.

The apparatus was working properly at the time of launching. A satisfactory number of spectra (170) were obtained of the ion composition of the ionosphere. A further check of the apparatus after the container had landed showed that it was still in working order.

The first ion spectra were obtained at an altitude of 105 km during the ascent, and the last at an altitude of 120 km during the descent.

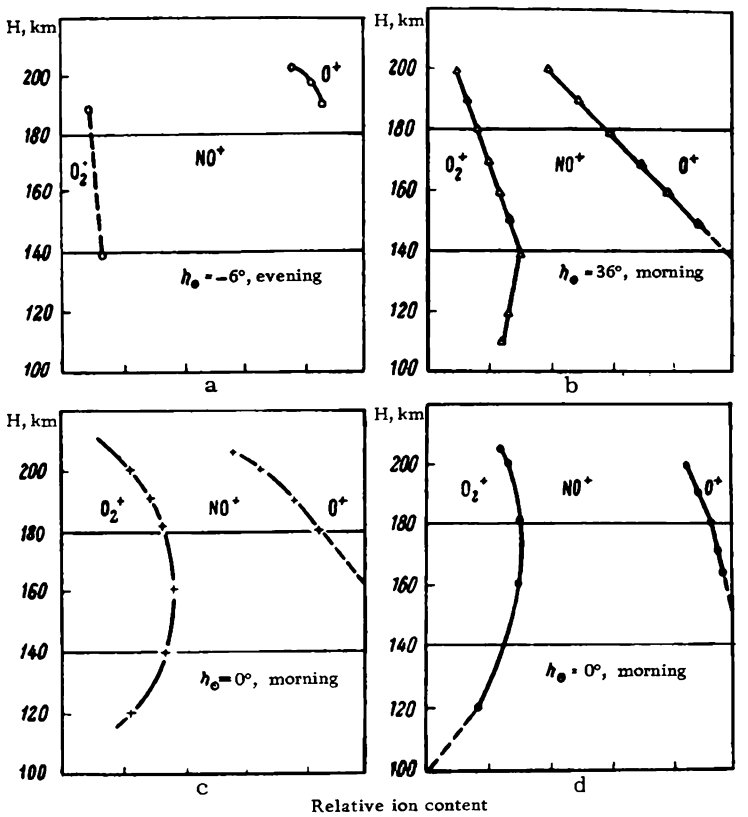

FIGURE 72. Composition of the ionosphere in the medium latitudes of the European territories of the Soviet Union

During this flight, three ions were found in the ionosphere, with mass numbers 16, 30 and 32 (O^+, NO^+ and O_2^+). Between 105 and 190 km, the concentration of O^+ and O_2^+ did not exceed 20 % of the concentration of NO^+,

which predominated at all altitudes (105–206 km). O^+ ions were recorded between 190 and 206 km, and their concentration was observed to increase in this range. Since no systematic shift of the ion peaks in the spectrograms was observed during this flight, we can conclude that the potential of the container remained constant to within ± 2V.

The results obtained from this flight are plotted in Figure 72a.

Ascents of geophysical rockets in the medium latitudes of the European territories of the Soviet Union, 2 and 13 August 1958

The same mass spectrometer was used for the Soviet ascents in 1958 as for the above-mentioned ascent. In these ascents, the containers reached an altitude of about 200 km. In both ascents the mass spectrometer worked properly, allowing a large number of mass spectra of the positive ions to be obtained between 110 km and the maximum altitude reached by the container, both during the ascent and descent. The data obtained allowed the ion "cross section" of the ionosphere to be determined in the region covered by the ascent.

The overall picture obtained agreed with that obtained previously (both in the Soviet Union and abroad). The main ion in the lower layers of the ionosphere is NO^+, while O^+ appears in measureable amounts from 150–160 km and increases rapidly with height; O_2^+ is present in appreciable concentrations mainly in the lower layers of the ionosphere (100-150 km). The concentration of O_2^+ has a tendency to decrease during the day. The results obtained from the 1958 ascents are plotted in Figure 72b and c.

Ascent of geophysical rocket in the medium latitudes of the European territories of the Soviet Union, 22 July 1959

The mass spectrometer which allows us to analyze the light gases (see Figure 62) was used in this flight.

The new apparatus was mounted in the same type of container as the old one (Figure 63). On 22 July 1959 this container reached an altitude of about 200 km. The apparatus worked satisfactorily, and a large number of mass spectra of positive ions were obtained. The results are plotted in Figure 72d.

The data obtained concerning the ions of the light gases (hydrogen and helium) during this ascent are of considerable interest. These ions were not detected by the apparatus up to an altitude of 200 km. Istomin concluded from this that in the region under investigation the concentration of hydrogen and helium ions cannot exceed 10^3 ions per cm^3*.

Conclusion

The experiments carried out to determine the content of the various positive ions in the ionosphere can be divided into two main groups: 1) the preliminary experiments, up to and including the flight of the Aerobee-24,

* The American investigators came to a similar conclusion /137/.

and 2) the later experiments, three in Aerobee-Hi rockets and four in geophysical rockets.

The first group of experiments were characterized by unreliable and variable results. The case of the Aerobee-24, where no positive ions at all were found, is most strange. It is true that the ionic composition varies more than that of the neutral gases, but not so much that all the positive ions can become negative.

The other group of experiments, on the other hand, comprising seven experimental rocket ascents, gave a fairly uniform picture of the ionosphere (see Figures 71 and 72) despite the wide variation in place (Arctic, southern and medium latitudes) and time (day, night, summer, winter) of the ascents.

Assuming that the second group of experiments gives a true picture of the structure of the ionosphere (and this is confirmed by the further experiments in artificial satellites, see Chapter VI), we can describe the vertical distribution of its various components as follows.

The lower ionosphere is composed mainly of positive ions of mass 30 (nitric oxide, NO^+), except in the middle of the day, when considerable amounts of molecular oxygen ion O_2^+ are found at altitudes of 100–120 km. As the height increases, O^+ ions, which appear at altitudes of 140–150 km, take the place of NO^+ and O_2^+ ions, and rapidly increase in concentration, being the most abundant ion at altitudes above 200 km. It is difficult to say anything definite about the distribution of the minor constituents (eg., N_2^+ and H_2O^+) in the region investigated. As all the ascents of Aerobee-Hi rockets indicate, the question of the presence of ions of mass 18 (presumably water) in the upper atmosphere is particularly complex. We shall discuss this problem in more detail in Chapter VI, and we shall also examine the results obtained using artificial satellites. For the moment, we shall only note that it is difficult to explain the presence of such large amounts (about 1 %) of water ions at such high altitudes (150 km and more) by any general geophysical hypothesis.

Hydrogen and helium ions and ions of mass 17 (hydroxyl) are conspicuous by their absence from the ion spectra obtained in these experiments. This shows quite convincingly that hydrogen is not present in appreciable amounts at altitudes of 100–250 km.

Negative NO_2^- ions were found in the ionosphere each time a mass spectrometer capable of recording negative ions was sent up; it is therefore likely that this ion (and also certain other negative ions) is present (in small concentrations) in the Earth's atmosphere*.

* As mentioned above, the NO_2^- ions found in these experiments may however be a combustion product of the rocket fuel involved.

Chapter VI

INVESTIGATIONS OF THE IONIC COMPOSITION OF THE UPPER ATMOSPHERE USING RADIO-FREQUENCY MASS SPECTROMETERS MOUNTED IN ARTIFICIAL SATELLITES (SPUTNIKS)

1. The use of artificial satellites for the investigation of the Earth's upper and outer atmosphere

The advent of the artificial satellite opened a new era in the investigation of the upper atmosphere, the outer regions of the atmosphere and the cosmic space surrounding the Earth. The limits of investigation have been pushed back so far that at the moment it is difficult to grasp all the new possibilities open to investigators in many different fields, including those concerned with the composition of the Earth's upper and outer atmosphere.

The launching of the first Soviet "sputniks", loaded with many different scientific instruments, represented a new gigantic step forward in the conquest of high altitudes, only comparable (if at all) with the advance which was made when the investigation of the atmosphere passed from sounding balloons to high-altitude rockets. We must now therefore pay some attention to the ways in which the flight of a satellite differs from that of a normal experimental rocket (vertical ascent). We must also determine the position which satellite experiments occupy in the overall picture of atmospheric investigations.

The use of rockets for obtaining information on the upper atmosphere is limited by the very short length of time the rockets stay in the region under investigation; in the best cases, this time does not exceed 5-7 minutes. Moreover, with the aid of rockets it is at the present time difficult if not impossible to carry out simultaneous investigations from a sufficient number of different points on the Earth's surface, especially including regions which are difficult to reach.

One of the decisive advantages of experiments carried out in satellites is that the measuring equipment spends a long period of time in the layers under investigation. Together with the enormous velocity of the satellite (about 8 km/sec), this allows repeated and nearly simultaneous observations to be made at points tens of thousands of kilometers apart. The time interval between observations in the equatorial zone and near the poles need not exceed 20-30 minutes. The fact that the satellite repeatedly returns to the same zones (with a period of revolution of about 90 minutes) means that the atmospheric composition can be measured as a function of time, and therefore investigations can be carried out on the variations of the solar activity in the ultraviolet range of the spectrum or with regard to corpuscular

radiation. Similarly, the satellite should provide a good solution to the problem of investigating the diurnal and nocturnal composition of the atmosphere. If its orbit is chosen properly, in each 90 minutes of its flight the satellite will pass over parts of the Earth which are lit by the Sun and parts which are in shadow, so that both nocturnal and diurnal parameters of the atmosphere can be determined.

The satellite has one further considerable advantage over the rocket: its small volume and the care with which it is hermetically sealed mean that the evolution of gas from inside it will be minimum. Its long stay in rarified regions of the atmosphere allows its surface to become thoroughly degassed and, which is particularly important, also allows the internal surfaces of the measuring equipment to be degassed. For the investigation of the ionic composition of the atmosphere, this advantage has a considerable (albeit indirect) effect. It goes without saying that one satellite provides more information than a hundred rockets together. All these advantages of the satellite compared to the normal experimental rocket definitely make it the instrument par excellence (so far) for the investigation of the upper atmosphere and the regions of cosmic space nearest to the Earth.

However, the satellite also has a number of serious disadvantages, which prevent it from being a completely universal means of investigating the upper atmosphere. In the first place, as a result of the appreciable retardation caused by the atmosphere the satellite must have a perigee of at least 200–400 km if it is to remain in orbit for a long time. The very important region of the upper atmosphere from 60–200 km, where the "vital activity" of the atmosphere is concentrated, thus falls completely outside the range of satellite investigations. Secondly, the trajectory of the satellite is very complicated, so that despite its elongated orbit, which criss-crosses the atmosphere between the perigee and apogee, the satellite cannot (like the rocket) give a vertical cross section of the atmosphere above a given point on the Earth's surface. This latter fact greatly complicates the analysis of data obtained using satellites, in which effects of latitude and longitude are interwoven with altitude effects.

It follows that investigations carried out using satellites must be regarded as extensions of rocket investigations but cannot completely replace the latter, just as rocket investigations have not replaced sounding-balloon experiments entirely. Each range of altitudes has its own investigation methods, which are not used in other ranges, and in this sense the satellite is only one link in the chain of investigations.

2. Characteristics of the method of investigation

The flight velocity of a satellite is very high, being nearly an order of magnitude greater than the velocity of the molecules surrounding it. Moreover, the slow, random rotation of the satellite continually changes the orientation of the inlet of the analytical equipment with respect to the satellite's velocity vector. Since the inlet of the radio-frequency mass spectrometer is situated right at the surface of the satellite, these factors may give rise to a certain error in the measurement of the ionosphere parameter. Before describing the results obtained in satellite experiments,

we must thus pause for a detailed discussion of the problem of estimating the reliability of the data obtained.

*a) Disturbance of the gaseous medium caused by the satellite's flight**

During its flight through the rarefied upper atmosphere, the satellite produces a stream of molecules which move along with it at a very high velocity compared to that of the molecules of the surrounding medium. We may distinguish two sources of such molecules: emission from the satellite itself (desorption from the surface and escape from inside), and elastic collision with the molecules of the surrounding medium. Molecules from the first source move with a velocity of 8.5–9 km/sec with respect to the molecules of the atmosphere, the thermal motion of which can be neglected, while those from the second source move with a velocity of 13–16 km/sec. These effects disturb the atmosphere around the satellite, leading in the first place to a change in its density, in the second place to thermochemical reactions and ionization by collision, and in the third place to a "rear cone" of molecular shadow**, into which only the fastest molecules of the surrounding medium, and free electrons, can penetrate. Therefore for the reasons mentioned above, when the satellite is used for such experiments as measuring the ion composition, ion concentration and density of the air, the results obtained may not correspond to the real parameters of the undisturbed atmosphere.

Before analyzing the reliability of measurements carried out at the satellite's surface, we must make a number of preliminary remarks. We shall assume that:

a) molecules emitted from the surface of the satellite will lose half their velocity (on the average) on elastic collision with the practically stationary molecules of the surrounding air, and in inelastic collisions they will lose even more than half; they will therefore either lag behind the satellite or, if they undergo collision near the satellite, they may return to it;

b) the density of molecules emitted from the surface of the satellite is such that they hardly ever collide with one another, even at very short distances from the surface***;

c) if the molecules are emitted from a stationary body, the mean free path is the distance they have to travel from the body before colliding with a molecule of the surrounding medium. The situation is however different when the body which emits the molecules is itself in rapid motion. In this case, the molecules in the front hemisphere do not travel so far before their first collision, because the body itself moves after them. The distance which the molecules travel from the moving body before their first collision will be called the "escape path" here, and will be denoted by λ^*.

This "escape path" λ^*, and not the mean free path, determines the frequency of collisions at various distances from the moving body.

It may be shown that the "escape path" is related to the mean free path

* After our paper /127/.

** The cone of molecular shadow is caused by the fact that the velocity of the satellite is an order of magnitude greater than the thermal velocity of the molecules of the surrounding medium.

*** This fact is well known from experiments with molecular beams /128/, even for the case of very high emission densities.

in the medium through which the satellite moves by the following expression:

$$\lambda^* = k\lambda_{atm}. \tag{1}$$

The coefficient k depends on the velocity v_c of the satellite, the velocity v_M of the molecules and the angle φ between the velocity vector of the satellite and that of the molecules. In general, this relationship can be sufficiently well approximated to by the following formula:

$$k = \frac{v_M}{v_M + v_c}\cos^2\psi + \frac{v_M}{\sqrt{v_M^2 + v_c^2}}\sin^2\psi, \tag{2}$$

where the angle ψ is given by

$$\psi^2 = \frac{4\varphi^2}{\pi^2 - 4\varphi^2}.$$

At the extremes of this range $\left(\varphi = 0, \varphi = \frac{\pi}{2}\right)$, equation (2) gives

$$k_0 = \frac{v_M}{v_M + v_c}, \tag{3}$$

$$k_{\pi/2} = \frac{v_M}{\sqrt{v_M^2 + v_c^2}}. \tag{4}$$

For the majority of molecules emitted from the satellite, for which $v_c \gg v_M$, equations (3) and (4) are practically identical; these equations only differ in the case of molecules emitted at very high velocities, when

$$k_{\pi/2} = k_0\sqrt{2}\ (v_c = v_M).$$

For simplicity, we shall use equation (3) in all cases. We should note that when $v_c = 0$ (stationary body), equation (2) gives $k = 1$, i. e.,

$$\lambda^* \equiv \lambda_{atm};$$

d) in the free atmosphere at altitudes of 200–700 km, Maxwell's law for the distribution of the velocities of the molecules holds, and the mean free path of the molecules at these altitudes is given by the normal exponential law.

Effect of the molecular emission. Apart from increasing the concentration of molecules around the satellite, the molecular emission can also change the composition of the surrounding gas, since the energy of the emitted molecules (about 10 eV) is sufficient for them to dissociate or react with the molecules (or ions) with which they collide. We shall now discuss how the concentration of molecules and the frequency of their collisions in the neighborhood of the satellite are altered by the desorption of gas from the satellite's surface.

The concentration of molecules emitted by the satellite (number of molecules per unit volume) will decrease with increasing distance from the satellite, for two reasons:

a) as a result of collisions, which remove molecules from the stream of gas flowing out from the satellite,

$$N_x = N_0 e^{-\frac{x}{\lambda^*}}, \tag{5}$$

where N_0 is the number of molecules leaving the satellite's surface in unit

time; N_x is the number which travel a distance x without colliding, and λ^* is the "escape path";

b) as a result of the increasing volume which must be occupied by the escaping gas*.

Let us suppose that the satellite is a sphere of radius R, and let us consider the increase in concentration of molecules, emitted from the satellite's surface, in a thin spherical shell of thickness d, situated at a distance x from the satellite. This increase in concentration is given by:

$$\rho_x = \frac{N_x d}{v_M V}. \tag{6}$$

Substituting the value of the volume V of the shell calculated by elementary geometry and the value of N_x given by equation (5), we find:

$$\rho_x = \frac{N_0}{4\pi v_M} \cdot \frac{e^{-\frac{x}{\lambda^*}}}{(R+x)^2}. \tag{7}$$

Knowing R, N_0, v_M, v_0 and λ_{atm}, we can use equation (7) to calculate the increase in concentration at a distance x due to emission from the satellite. This number includes all the molecules reaching the shell of thickness d.

Since the molecules emitted by the satellite travel in straight lines and do not collide much with one another, it would be possible to keep all these molecules out of the measuring equipment by arranging its inlet so that it could not "see" any of the satellite's surface, were it not for the collision of these molecules with the molecules of the surrounding medium. These collisions (whose number is proportional to the density of the surrounding medium) cause some of the molecules emitted from the satellite to be deflected into the measuring equipment. Thus while the direct effect of the molecules from the satellite can be eliminated fairly easily, it is impossible to eliminate the indirect (scattering) effect. We must thus calculate the number of collisions which can return the emitted molecules to the measuring equipment.

According to equation (5), the number of directly emitted molecules passing the inner boundary of the layer of thickness d in unit time is given by:

$$N'_x = N_0 e^{-\frac{x}{\lambda^*}}. \tag{8}$$

Because of the collisions, the number of molecules leaving the outer boundary of this layer will be:

$$N''_x = N'_x e^{-\frac{d}{\lambda^*}}.$$

Substituting the value of N_x from equation (8) and putting $d = 1$ cm, we obtain

$$N''_x = N_0 e^{-\frac{x}{\lambda^*}} \cdot e^{-\frac{1}{\lambda^*}}. \tag{9}$$

The difference between equations (8) and (9) gives the number of molecules which undergo collisions in this layer, and which are thus reflected

$$N^* = N_0 \frac{e^{-\frac{x}{\lambda^*}}}{\lambda^*}.$$

* In fact, at short distances from the satellite the density will decrease as $\frac{1}{2}\left[1 - \sqrt{1 - \left(\frac{r}{R}\right)^2}\right]$. However, for our calculations we may use the $1/R^2$ law without too much error.

Using a relationship similar to (6), and the value of N^* given above, and also taking into account that the velocity v'_M of the returning molecules* differs from the velocity v_M of the directly emitted molecules, we can without difficulty calculate the number of reflected molecules formed per unit volume at a distance x from the satellite. However, unlike the case with the directly emitted molecules, which all came from a single source (the surface of the satellite), the reflected molecules are produced by an extended source, since collisions can occur wherever the directly emitted molecules occur. In order to find the total concentration of reflected molecules at a certain distance a from the satellite's surface, we must integrate over the volume of a cylinder of unit cross section, extending from a to infinity. In this way the concentration of reflected molecules at a distance a from the satellite's surface (β_a) is

$$\beta_a = \frac{N_0}{4\pi v'_M \lambda^*} \int_a^\infty \frac{e^{-\frac{x}{\lambda^*}}}{(R+x)^2}\, dx. \tag{10}$$

With a coordinate system based on the satellite, the velocity v_M of the reflected molecules is appreciably greater than the absolute value of the velocity of the directly emitted molecules. We may therefore put

$$|v'_M| = n\,|v_M|, \qquad n > 1.$$

If the inlet of the measuring equipment is at the surface of the satellite, we must carry out the integration from zero to infinity:

$$\int_0^\infty \frac{e^{-\frac{x}{\lambda^*}}}{(R+x)^2}\, dx = \frac{1}{R} + \frac{e^{\frac{R}{\lambda^*}}}{\lambda^*}\,\mathrm{Ei}\left(-\frac{R}{\lambda^*}\right). \tag{11}$$

At altitudes greater than 200 km, where $\lambda^* \geqslant R$, the second term on the right-hand side of (11) can be neglected, so that (10) becomes:

$$\beta_0 = \frac{N_0}{4\pi v_M \lambda^*} \cdot \frac{1}{R}. \tag{12}$$

According to (7), the concentration of directly emitted molecules at the satellite's surface will be

$$\rho_0 = \frac{N_0}{4\pi v_M} \cdot \frac{1}{R^2}. \tag{13}$$

Dividing (12) by (13), we find:

$$\frac{\beta_0}{\rho_0} = \frac{v_M R}{v'_M \lambda^*}. \tag{14}$$

Equation (14) shows that the number of reflected molecules β_0 depends on the radius of the satellite, the ratio of the velocities of the directly emitted and reflected molecules, the escape path, and the concentration of molecules emitted by the satellite. Other things being equal, the satellite with

* For the measurements carried out in the satellite, the only reflected molecules which are harmful are those produced by collisions in a cylinder of radius R, whose axis is parallel to the direction of motion of the satellite. We now neglect the effect of diffusion and assume that all the reflected molecules produced in this cylinder return to the satellite. This assumption should not introduce a large error, since the loss of molecules through the side walls of the cylinder will be compensated by a similar flow of molecules from outside.

the smallest radius will give the lowest percentage of reflected molecules.

Table 28 shows how the ratio β_0/ρ_0 varies with height (for $R = 100$ cm and $n = 10$).

TABLE 28

Height, km	λ_{atm}, cm	λ^*, cm	β_0/ρ_0
500	10^6	$5 \cdot 10^4$	$2 \cdot 10^{-4}$
300	10^5	$5 \cdot 10^3$	$2 \cdot 10^{-3}$
200	10^4	$5 \cdot 10^2$	$2 \cdot 10^{-2}$
150	$2 \cdot 10^3$	$1 \cdot 10^2$	$1 \cdot 10^{-1}$

The following conclusions can be drawn from the results of Table 28:

1) The disturbing effect of reflected molecules, which cannot be prevented, has however a negligible influence on determinations of the density or chemical composition of the surrounding gas at altitudes above 200 km, compared to the influence of the directly emitted molecules. The reliability of measurements carried out from a satellite thus depends on the success with which the directly emitted molecules are prevented from getting into the measuring equipment together with the molecules of the free atmosphere at a given height. It should be mentioned that, with a constant value of ρ_0 (constant emission of gas from the satellite), the value of the ratio β_0/ρ_{atm} (where ρ_{atm} is the concentration of molecules in the undisturbed atmosphere) does not vary with height.

2) Below 150 km we have a different picture: here an appreciable number of the molecules emitted by the satellite undergo collisions in the immediate vicinity and may be returned to the satellite.

We shall now carry out a number of numerical calculations on the basis of the above. For this purpose we must make a reasonable estimate of the number of molecules N carried by the satellite into the upper atmosphere, and we must also give the time T taken for these molecules to be emitted from the satellite's surface. Assuming that a monomolecular absorbed layer contains 10^{15} molelcules per cm^3, and that the actual layer of absorbed molecules on the surface of the satellite is say 50 molecules thick, and further that the overall surface area of the satellite is 10^6 cm^2, we find for the total number of absorbed molecules:

$$N = 10^{15} \cdot 10^6 \cdot 50 = 5 \cdot 10^{22}.$$

We shall take the desorption time T as equal to the time taken for one revolution of the satellite round the Earth, i. e., about 5000 sec*, and shall assume the desorption to be uniform. This is not in fact true, but the error introduced increases the effect and does not diminish it. We thus find

$$N_0 = \frac{N}{T} = 10^9 \text{ mol/sec.}$$

* As will be seen later, this assumption is quite close to the actual value.

Further, for a solution of equation (7), we substitute the following values:

$$R = 100\,\text{cm},\quad v_M = 4 \cdot 10^4\,\text{cm/sec},\quad v_c = 8 \cdot 10^5\,\text{cm/sec},\quad k = 5 \cdot 10^{-2}.$$

The molecules directly emitted by the satellite form a sort of cloud around it. Figure 73 shows the variation of the density of this cloud with distance from the satellite's surface, at various altitudes (100, 150 and 300 km). It can be clearly seen from the graph that as the height increases,

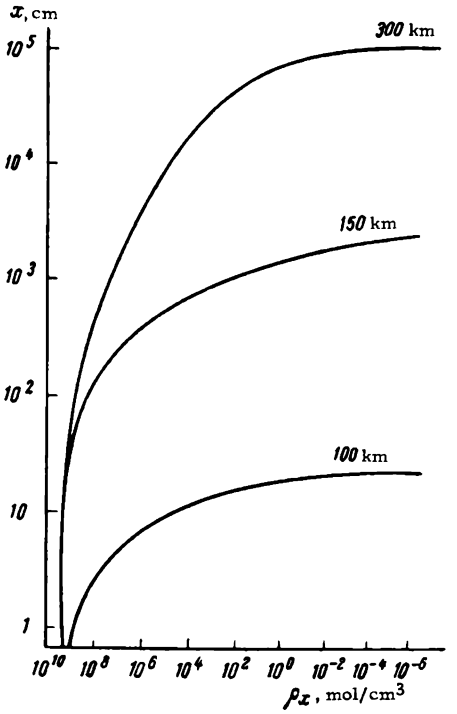

FIGURE 73. Density ρ_x, of molecular "cloud" as a function of the distance x from the satellite's surface

the density of the cloud falls off more slowly away from the satellite's surface. Thus, at an altitude of 300 km, the concentration of emitted molecules remains practically constant in a region a meter wide round the satellite. At lower altitudes, this region is considerably smaller.

The above graph allows us to make some recommendations about the positioning of the measuring equipment on the satellite. When the satellite is to make flights at altitudes of 250 km or more, the inlet of the measuring equipment should project from the surface of the satellite by at least 2–3 meters. As we have already seen, proper positioning of the measuring equipment — with its inlet projecting above the surface — provides sufficient screening against the directly emitted molecules.

The situation is completely different with the highly dangerous reflected molecules. In order to reduce their harmful effect, it is very important that the inlet of the measuring equipment should extend a certain distance from the satellite's surface. According to equation (10), each ten centimeters

between the inlet and the satellite's surface (the distance a in equation (10)) causes a considerable decrease in the number of reflected molecules, since the whole region between the inlet and the satellite's surface, which is most rich in reflected molecules, is excluded from the measurements. Ideally, the distance between the inlet of the measuring equipment and the satellite's surface should be roughly equal to the radius R of the satellite, In this case, practically all the molecules directly emitted by the satellite would be reflected before they reached the inlet, and would not cause any error in the measurements.

The maximum permissible leak (loss of gas from inside the satellite), at which the undisturbed parameters of the atmosphere can be measured, can be estimated in a similar way to that used above for considering the evolution of gas from the satellite's surface. If we assume that all the flow of gas from the interior of the satellite takes place from its center then we see from equation (7) that the maximum permissible leak is about 10^{19} mol/sec. As we have seen above, the value of the permissible leak is the same at all altitudes, if the emission of gas is constant. The above value of the permissible leak only holds if the directly emitted molecules cannot reach the measuring equipment. If the measuring equipment does admit directly emitted molecules, the error in the measured density may be very considerable, and will increase in inverse proportion to the density of the surrounding medium. Thus, if the conditions mentioned above are satisfied, the evolution of gas from the satellite, even including a large constant leak, will not have any appreciable effect on the measured values of the density and composition of the surrounding gas.

The greatest influence on the surrounding gaseous medium is exerted by the molecules which suffer elastic collisions with the surface of the satellite. These molecules, which acquire a velocity of 15-16 km/sec and an energy of about 30 eV, can easily cause ionization or other changes in the molecules which they encounter, whose number is proportional to the density of the medium. The number of these fast reflected molecules at a distance x from the satellite's surface can be estimated from equation (7), if we insert appropriate values of N_0, $v_м$ and k. If we consider an altitude of about 200 km, where the gas concentration is $\nu = 10^{10}$ mol/cm^3, then the number of molecules colliding per second with a satellite of cross-sectional area 3 m^2 will be $N_0 = 10^{10} \cdot 10^5 \cdot 8 \cdot 3 \cdot 10^4 = 2.4 \cdot 10^{20}$ mol/sec ($v_м = 8 \cdot 10^5$, $k = \frac{1}{\sqrt{2}} \approx 1$). Substituting these values in equation (7) and multiplying by two (in this case, the molecules only collide with the front hemisphere of the satellite), we obtain the additional concentration due to collisions of molecules with the satellite's surface, at an altitude of 200 km, this additional concentration at the satellite's surface will amount to $2 \cdot 10^9 - 3 \cdot 10^9$ mol/cm^3. This concentration will decrease with increasing height, but the ratio of this concentration to the concentration of molecules in the free atmosphere will remain constant. The change in the density of the surrounding medium due to fast (reflected) molecules is thus even more insignificant than the change due to the slow molecules (emitted from the satellite's surface).

If the molecules reflected from the satellite have a velocity $v_м = v_c = 8$ km/sec, then $k = 1$ and $\lambda^* \equiv \lambda_{atm}$ (we assume that on nonelastic collision with the molecules of the atmosphere, the fast molecules lose a large part of their velocity); for an altitude of 200 km, where $\lambda_{atm} = 10^4$ cm, we find

from equation (14), taking $n \approx 1$, $\beta_0/\rho_0 = 10^{-3}$, i.e., the concentration of reflected particles at the satellite's surface is $\beta_0 = 2 \cdot 10^6$ mol/cm^3. This concentration will decrease more rapidly with increasing height than the concentration of the surrounding medium.

We must now estimate the harm the collisions of these particles can do to the measurements of the ionization, composition and density of the undisturbed atmosphere carried out in the satellite. Assuming with Herlofson /129/ that the ionization coefficient for such collisions is $\alpha = 10^{-4}$, we find that 1 cm^3 of air near the satellite's surface will contain about 100 extra ions, which is negligible compared with the natural concentration of ions (10^5–10^6 ion/cm^3). The effect of thermochemical reaction on the measured composition of the atmosphere is also very small, even if we assume that nearly every collision of a fast molecule gives rise to such a reaction; Finally, the change in the density round the satellite as a result of these reflected molecules will also be negligible, even at an altitude of 200 km ($2 \cdot 10^6$ mol/cm^3, compared with 10^{10} mol/cm^3 in the atmosphere).

*b) The influence of the nonoriented flight of the satellite and the charge which it acquires on the recording of the ion spectra obtained**

The high velocity of the satellite, which we have mentioned in the previous section, also has a direct effect on the measurements made by the radio-frequency mass spectrometer. Since the mass spectrometer is mounted in a moving body, the velocity of the atmospheric ions relative to the measuring equipment will contain a directed (nonrandom) component equal to the velocity of the satellite, apart from their (random) thermal velocity. Because of this velocity, $v = 8 \cdot 10^5$ cm/sec, ions of mass number M and charge $q = 4.8 \cdot 10^{10}$ c. g. s. units have a certain energy, equivalent to that due to accelerating voltage

$$\Delta V_v = 300 \frac{M m_0}{2q} v^2, \tag{1}$$

where $m_0 = 1.67 \cdot 10^{-24}$ g, which is 1/16 of the weight of an oxygen atom. For ions of mass number 16, this velocity of $8 \cdot 10^5$ cm/sec corresponds to an energy of 5.35 eV, and for ions of mass number 30 to 10 eV. As a result of this, the retarding potential of the equipment is lowered by a different amount for ions of different masses, this amount being numerically equal to the energy of the ions in electron volts. Moreover, as has been shown by analysis of the spectra obtained, the satellite has a negative potential of a few volts, which leads to a further reduction of the effective retarding potential by an amount which is the same for all atmospheric ions.

As a result of the lowering of the effective retarding potential due to these two effects, the sensitivity of the mass spectrometer is increased several times, more for heavy ions than for light ones, and the mass resolution is consequently decreased to about half that found for the equipment in the laboratory. If the equipment is designed for a resolution $R = \frac{M}{\Delta M} = 20$ in the region around mass number 20 (where as usual M is the mass number of the peak and ΔM is its width at the base, expressed in atomic mass

* After the publications /122, 132/.

units), then in the spectra obtained with the atmospheric ions the resolution as defined for the base width of the peak in the region of mass numbers 14–16 will be equal to 7–10. This means that a peak in the region of light gases ($M = 16$) will be completely separated from the neighboring peak if the distance between the peaks is two or more mass units. In the region of heavy gases ($M = 30$), peaks separated by two mass units will not be completely resolved. This must be borne in mind when interpreting the experimental results.

Because of the presence of harmonic peaks in the spectra, the dynamic range of the apparatus is appreciably widened on the high-intensity side. Since the peak height of the harmonic of mass 16 is equal to 0.1 of that of the main peak, then when peak 16 is sufficiently intense to saturate the low-sensitivity output of the amplifier (current exceeds 10^{-8} A), the concentration can be estimated from the height of the harmonic peak.

The mass numbers of all peaks in the spectra are shifted towards low mass numbers because of the effect of the velocity of the satellite and its negative charge. It will be remembered that in the radio-frequency mass spectrometer the mass resolution is produced by a saw-tooth variation of the negative accelerating voltage. Under laboratory conditions the mass number of a peak is determined by the formula:

$$M = \frac{V}{K}, \tag{2}$$

where M is the mass number of the peak in atomic mass units, V is the value of the resolving voltage in volts at the moment the peak is observed, and K is an apparatus constant, equal to 7.2 V per atomic mass unit.

When the apparatus is used in a satellite, the negative resolving voltage V is increased by an amount ΔV_v corresponding to the energy in electron volts of the ion in question moving with a velocity of $8 \cdot 10^5$ cm/sec, and by a further amount φ, the negative potential of the satellite. Equation (2) can thus be written in the form

$$M = \frac{1}{K}(V + \Delta V_v + \varphi) = M_{\text{rec}} + \Delta M_v + \Delta M_\varphi, \tag{3}$$

where M_{rec} is the mass number of the peak as read off from the recorded spectrum, ΔM is the correction for the velocity of the satellite and ΔM_φ is the correction for its charge.

As may be seen from equation (1), the value of ΔV_v itself depends on the mass number of the ion; the expression for the mass number of the peak may therefore be written:

$$M = \frac{1}{K}\left(\frac{V + \varphi}{1 - \frac{300 M_0}{2K}}\right) = \frac{M_{\text{rec}} + \Delta M_\varphi}{1 - \frac{300 M_0 v^2}{2qK}}, \tag{4}$$

or finally, substituting numerical values for the variables:

$$M = \frac{1}{K}\left(\frac{V + \varphi}{1 - \frac{0.331}{K}}\right) = \frac{M_{\text{rec}} + \Delta M\varphi}{0.954}. \tag{5}$$

As may be seen from equation (5), for a given radio-frequency mass spectrometer the shift in the mass peaks due to the satellite's velocity should be 0.74 atomic mass units at mass 16 and 1.39 atomic mass units at mass 30.

When the orientation of the inlet of the mass-spectrometer tube changes with respect to the velocity vector of the satellite, the conditions under which the ions enter the apparatus are considerably changed. If the tube points backwards, the inlet will be in the region of "molecular shadow" which we have already mentioned. In this case, only a very small number of fast ions manage to enter the analyzer, which is not sufficient for the apparatus to work normally. In practice, the mass spectrometer will not record the ions of the ionosphere. If the tube points forward (i. e., if the angle between the velocity vector and the tube is 0°), this is the best situation for operating the apparatus both as regards reducing to a minimum all possible effects discriminating between ions of different masses, and as regards the amount of ions entering the mass-spectrometer tube. As the angle between the tube and the velocity vector increases, the amount of ions entering the apparatus falls off, while the discrimination effects increase.

It follows that the mass spectrometer should be fitted in the satellite so that when the latter is properly oriented the inlet of the apparatus points along the velocity vector, and is out of the molecular shadow.

3. Investigations of the ionic composition of the upper atmosphere

Consideration of the potentialities of the mass spectrometer makes it clear that this instrument would be suitable for making measurements from an artificial satellite. A radio-frequency mass spectrometer was therefore mounted in the third Soviet satellite, and with its aid V. G. Istomin obtained

FIGURE 74. The radio-frequency mass spectrometer installed in the third Soviet Earth satellite

1–electronics of mass spectrometer; 2–plug connection blocks; 3–connecting cables; 4–metal analyzer tube; 5–inlet of tube; 6–flange for hermetically sealing analyzer tube in body of satellite; 7–preamplifier.

a great deal of new and interesting information about the composition of the ionosphere*.

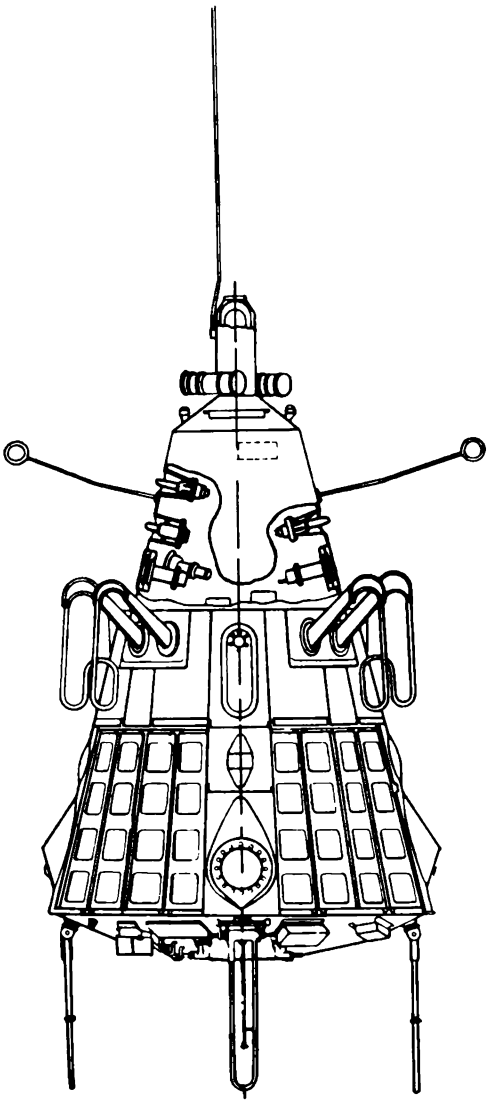

FIGURE 75. Diagram of the third Soviet Earth satellite

Experimental conditions. The radio-frequency mass spectrometer shown in Figure 74 was fitted in the third artificial Earth satellite, which was launched on 15 May 1958. As is known, a "sputnik" is a complicated piece of equipment, with many projecting parts (Figure 75); in accordance with the considerations given in section 2a of this chapter, therefore, the

* This is an account of the work of V. G. Istomin /122, 131, 132/, which is so far unique of its kind.

inlet of the mass spectrometer was situated so that as few gas-emitting surfaces as possible were in its field of view.

In order to prevent the sensitive equipment at the surface of the satellite (including the mass spectrometer grids) from the effects of high temperatures and pressure during its passage through the dense layers of the atmosphere before arriving in orbit, the satellite was enclosed in a protective cone. This cone consisted of several parts, which were automatically discarded when the satellite was separated from the last stage of the rocket, i. e., when it was already in orbit. This moment is sketched in Figure 76.

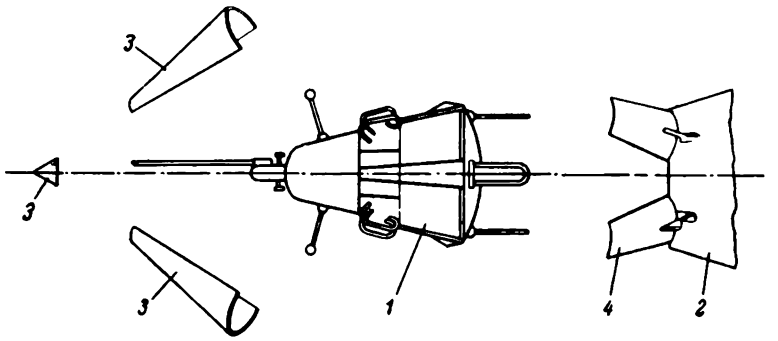

FIGURE 76. Moment at which the container with scientific equipment leaves the carrier rocket (sketch)

1—container with scientific equipment ("sputnik"); 2—carrier rocket; 3—various parts of the protective cone; 4—screens separated from the satellite.

At this moment, the satellite inevitably acquired a certain rotational motion and started slowly precessing about its velocity vector.

The mass spectrometer used for this experiment was designed to record only positive ions. The apparatus was set into operation when the protective cone was jettisoned. The mass spectrometer was switched on and off by means of a specially programmed mechanism controlled by radio signals. The apparatus was switched off periodically in order to save the power supply during those periods when the information from the mass spectrometer could not be picked up by the special receiving stations.

During the period of operation of the apparatus, from 15 to 25 May 1958, about 15,000 mass spectra of positive ions were obtained from altitudes of 225–980 km. The measurements were made in the northern hemisphere between 27 and 65° north latitude (in regions where direct radio observation was possible), mainly in the morning hours (from 0700 to 1100 hours, Moscow Time). At the time when the measurements were made, the satellite had a potential of about 3 V.

Identification of the spectra. All the material collected during the above-mentioned period can be divided into two parts: the initial results, when the gases (contamination) evolved by the surface of the satellite were clearly recorded by the mass spectrometer, and the final results when the degassing of the satellite was already complete and the apparatus only recorded atmospheric ions.

It may be mentioned that the first part was limited to the first two or three orbits of the satellite around the Earth; all the rest of the material

belonged to the second part. During the satellite's first few orbits, the mass spectrometer recorded, apart from the atmospheric ions, large amounts of water ions (mass number 18). Thanks to the satellite's rotation and the displacement of the ion peaks along the mass scale (the peaks of the contaminating ions are hardly displaced at all, while the atmospheric ion peaks are displaced towards the low-mass side), it was possible to show that the water ions which were recorded belonged to the ions of the contaminating gases. The variation of the water-ion current with time confirmed this: this current fell off steadily with time during the first three revolutions, and was only faintly recorded by the end of the third.

The problem of the ionization mechanism of the water molecules carried up by the satellite to the outer atmosphere is of particular interest. It is worth mentioning in this connection that the water ions are recorded even at moments when the inlet of the mass spectrometer is in a region of deep molecular shadow, i. e., when practically none of the atmospheric ions can reach the apparatus*.

Apart from the presence of large amounts of water during the satellite's first orbits, the material gathered at the beginning of the flight did not differ in principle from that obtained later. In both groups of spectra, a large number of ion peaks were found. This is because the spectrograms contained spurious (harmonic) peaks, due to components which were already recorded elsewhere in the same spectrum. Before proceeding to identify the spectra obtained, it was therefore necessary to separate the spurious (harmonic) peaks from the main ones. The harmonic peaks were eliminated with sufficient reliability and accuracy, and the identification of the remaining (main) peaks gave the final results.

The principal atmospheric ion peak in all spectrograms was that of the atomic oxygen ion (O^+), the next one in intensity being that of atomic nitrogen (N^+). Near the perigee (at an altitude of about 225–250 km), ion-current peaks corresponding to N_2^+, O_2^+ and NO^+ were observed. The strongest of these three peaks was that due to NO^+. And finally, all spectra contained a weak peak of mass 18.

Since the ions of mass 18 behave completely differently during the first few orbits than in subsequent orbits, we must consider this effect in greater detail. As we have already mentioned, the variation with time of the intensity of the peaks of mass number 18 during the first three orbits made it reasonable to assume that these peaks were due to water ions picked up by the satellite during its passage through the lower levels of the atmosphere. The variation of the intensity of these peaks with time after the first three orbits is completely different, exactly following the variation of intensity of the peaks due to ions of atmospheric origin, subject to the same mass shift and showing the same variation (a periodic rise and fall) due to the precession of the satellite. It may thus be concluded without any doubt that the ions of mass 18 recorded after the first three orbits must be of atmospheric origin.

What is the nature of these ions? The most obvious assumption is that these "mystery" ions are molecular water ions (H_2O^+), but the presence of appreciable amounts of water ions (about 0.2 %) at such high altitudes (225-500 km) is certainly most unexpected. On the one hand, it is highly improbable that water

* Progress is at present being made in clarifying the ionization mechanism (a very probable mechanism is overcharging, although other possibilities are also theoretically possible).

molecules can be carried to such high altitudes from the lower atmosphere by mixing or diffusion; and on the other hand it is equally improbable that water molecules should be able to remain undissociated at such high altitudes for long periods of time, since the solar radiation with $\lambda < 2400$ Å, which has the effect of dissociating water molecules, can penetrate freely down to 100 km above the Earth.

If we suppose that the water molecules are formed by some kind of photochemical reaction in the upper atmosphere, its presence at these altitudes being the result of a dynamic equilibrium between its formation and its dissociation, then there should be an excess of the dissociation products, H and OH, at the altitudes in question. The OH ion is however completely absent from the spectra of the positive ions (although the apparatus used does not allow the peaks of mass 17 and 18 to be separated, it would be quite possible to detect the harmonic peaks of ions of mass 17: but such peaks are absent from the spectra). This indicates that ions (and molecules) of water are not present in appreciable concentrations at these altitudes*. A simple and obvious explanation for the presence of this mystery ion of mass 18 was offered by V. G. Istomin /131/, who suggested that the ion in question might be that of a heavy isotope of oxygen, O^{18}. In nature, the concentration of this isotope is 0.2 % of that of normal atomic oxygen, O^{16}. The excellent agreement between the ratio of the ion currents $i_{18}/i_{16} = (0.15 \pm 0.05)$ % and the above-mentioned ratio $O_{18}/O_{16} = 0.2$ % leaves no doubt that we are really dealing with atomic oxygen ions here.

Distribution with height. The experiments carried out in the satellite not only provided information about the chemical composition of the ionosphere at high altitudes, but also indicated the laws governing the distribution of the ions with height. Despite the great difficulty of separating altitude effects from latitide-longitude effects, in some cases this proved possible. For example, Table 29, taken from one of Istomin's publications /121/, shows the ratio of the ion currents of atomic nitrogen and atomic oxygen at various heights.

TABLE 29

Height, km	230	250	255	285	385	460	650	750
i_{N^+}/i_{O^+}	0.037	0.030	0.035	0.045	0.060	0.060	0.070	0.060

In Figure 77 the ratio of the ion currents of atomic nitrogen and atomic oxygen are plotted against height on the basis of mass-spectrometer data for 12 orbits between 18 and 24 May 1958. The author considered the spread of the experimental points in this graph, ±2–3 %, to be due to real changes taking place in the ionosphere from day to day. The separation of heavy ions with height was also demonstrated. The relative intensities of the ion peaks of molecular oxygen, O_2^+, nitrogen, N_2^+ and nitric oxide, NO^+, reached a maximum near the perigee (about 230 km). Here the intensity of the NO^+ peak was 25–35 % that of the O^+ peak; the intensity of the O_2^+ peak was 7–12 % and that of the N_2^+ peak only 2–3 %. The ion currents of NO^+ and N_2^+ were traced up to altitudes of about 400–500 km, where they were found to be roughly the same, and equal to about 0.1–0.2 % of the ion current

* It is even less likely that ammonium ions, NH_4^+, which also have a molecular weight of 18 should be present in the atmosphere at high altitudes.

of O^+. Molecular oxygen disappeared at a somewhat lower height (about 400 km). Above 500 km, therefore, the ionosphere may be taken (with an accuracy of 0.1 %) to be composed of atomic oxygen and nitrogen.

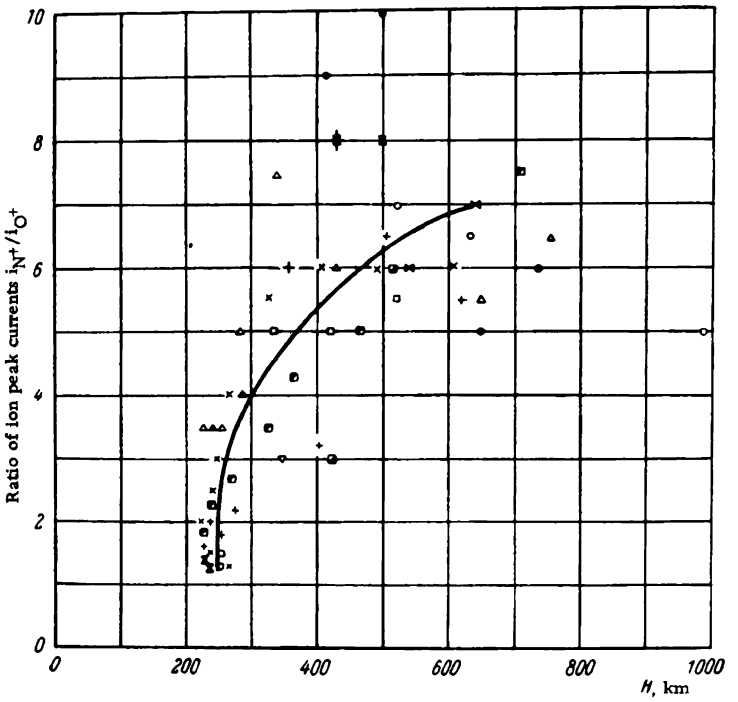

FIGURE 77. The ratio of the ion currents of atomic nitrogen and oxygen as a function of height

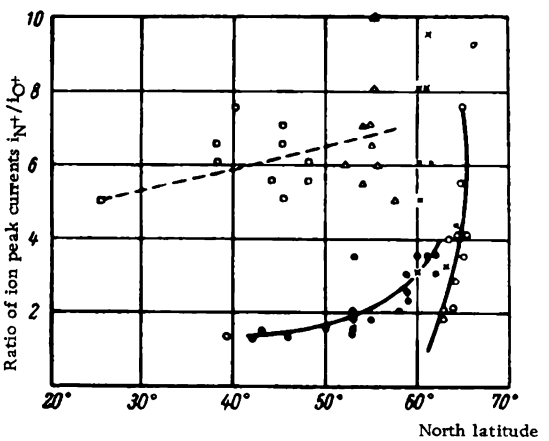

FIGURE 78. The ratio of the ion currents of atomic nitrogen and atomic oxygen as a function of latitude

●–225-250 km; O–251-350 km; ×–351–450 km; Δ–451-600 km; □–601-980 km.

Distribution with latitude. Processing of the spectrograms obtained also gave some information about the distribution of the ions in the ionosphere with latitude. The ratio of the currents N^+/O^+ is plotted in Figure 78 as a function of the latitude. It is difficult to separate the latitude effect from the altitude effect here, but for altitudes between 230 and 450 km it can be clearly seen that as the latitude increases, the amount of atomic nitrogen ions increases compared to the atomic oxygen ions. The relative ion currents of the heavy ions O_2^+, NO^+ and N_2^+ (with respect to O^+) also show a characteristic dependence. The variation of these ions with height and latitude combined is shown in Figure 79. Inspection of these curves shows that they can all be divided into two branches around the perigee: a southern one (1–2) and a northern one (3–7). The southern branch is always lower than the northern one, indicating a dependence of the relative concentrations of NO^+, N_2^+ and O_2^+ on latitude. As the latitude increases, the concentration of these ions compared to O^+ also increases.

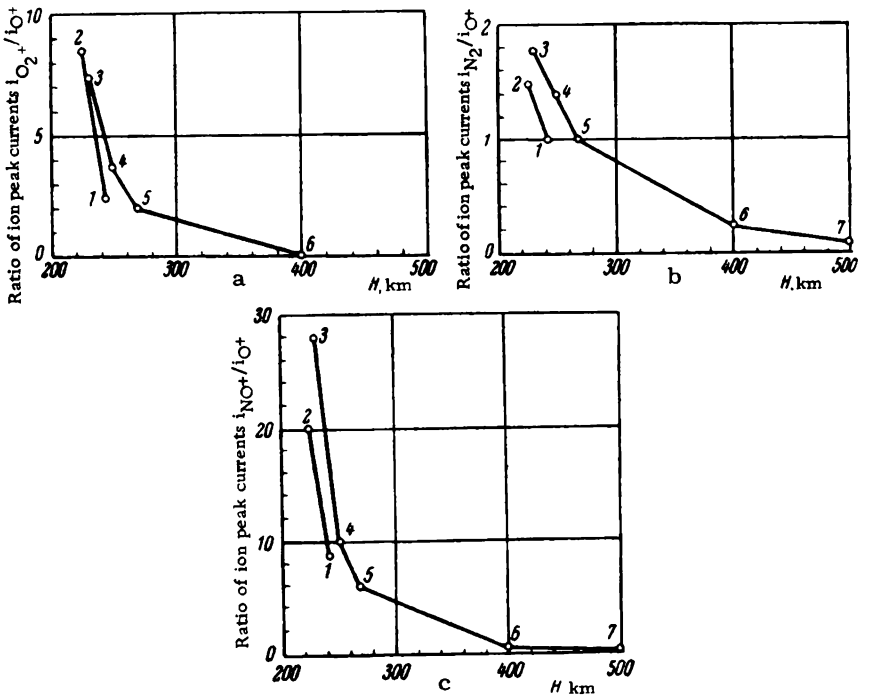

FIGURE 79. Combined latitude and height dependence of the ion-current ratios of molecular oxygen and atomic oxygen (a), molecular nitrogen and atomic oxygen (b) and nitric oxide and atomic oxygen (c)

4. Discussion of results

The unique information obtained using the mass spectrometer mounted in the sputnik has considerably broadened and enriched our knowledge of the chemical composition of the ionosphere. The sputnik's rotation and its rapid motion made for a reliable separation of the ions of the gaseous contaminations and the ions of the atmosphere proper, thus considerably

increasing the reliability of the results obtained. The care with which the experiments were carried out also contributed to the reliability of the data.

Since the perigee of the third Soviet satellite was at altitudes which had been explored by rockets, it was possible to compare the two sets of results. Complete agreement was found.

One fact which stands out from the results is that the ionic composition of the ionosphere changes with height. At these high altitudes, where collision between particles is relatively rare, the distribution of the gaseous particles with height is again appreciably affected by the law of gravitational separation of gases according to their weight. It is true that this law is considerably complicated by the circumstance that the particles in question are electrically charged, but the fact remains that the relative number of light particles increases with height. This may be particularly clearly seen, as V. G. Istomin showed, from the variation of the ratio of the isotopic oxygen ions $[O^{18}]/[O^{16}]$ with height (Table 30).

TABLE 30

Height, km	230	240	245-300	300-500
O^{18}/O^{16}	0.15 ± 0.02%	0.15 ± 0.03%	0.13 ± 0.02%	0.10 ± 0.026%

These figures may be taken as evidence of gravitational separation, since the other factors which would affect the distribution of oxygen atoms with height, such as cosmic radiation, photochemical reactions, etc., will be the same for both isotopes and cannot upset the general picture of their gravitational separation.

This separation is also found with all the other ions observed during these experiments, and may be seen particularly clearly from the distribution of the ions of atomic nitrogen and atomic oxygen.

The heavier molecular ions such as O_2^+, N_2^+ and NO^+ also show this effect, but less clearly, since at the relatively low altitudes where these ions are formed in appreciable quantities they are subjected to many effects other than that of gravitational separation which determine the "life" of the ionosphere at these altitudes.

The change of the concentration of the various components of the ionosphere with latitude is also very interesting. As we have mentioned, this effect consists in a fall with increasing latitude of the ion current for the main ion at high altitudes (atomic oxygen) with respect to the ion currents for all the other ions in the ionosphere. In other words, the polar regions of the ionosphere are relatively poor in atomic oxygen ions. This latitude effect seems to indicate that the ionization mechanism leading to the formation of the ionosphere varies somewhat with the latitude.

Near the equator, the main factor in the formation of the ionosphere is the ultraviolet radiation from the Sun, while near the poles this factor is joined by corpuscular radiation, the particles of which may have very high energies (e. g., the particles from the radiation belts). These particles will cause an increase in the ionization of the hardly ionizable components of the ionosphere at high altitudes and high latitudes, and possibly the dissociation of nitrogen molecules, which are very little dissociated by solar radiation. As a result of this, the relative amount of atomic nitrogen ions compared to the atomic oxygen ions may be greater near the poles than near the equator.

CONCLUSION

We have now come to the end of our account of all the main experimental work on the composition of the atmosphere; it only remains for us to sum up.

First of all, we must sketch the general picture of the composition of the atmosphere which, at present, is based on the experimental results.

The atmosphere from the Earth's surface to an altitude of about 15–20 km consists of a mixture of many gases; its composition is constant to a very high degree of accuracy*. This constancy of composition, which is due to intensive mixing effects (winds, turbulence), is found not just at certain particular spots on the globe, but over the whole surface of the Earth. This very remarkable fact was established beyond any doubt by a series of "world-wide" investigations, which we described in the first chapters of this monograph: samples taken from widely differing points of the globe, over land or sea, inhabited regions or barren wastes, plains or high mountains, all showed the content of oxygen and nitrogen to be constant to within the high degree of accuracy offered by modern analytical methods. Particularly striking in this connection is the behavior of such components of the Earth's atmosphere as the light gas helium and the heavy carbon dioxide, the supply of which to the atmosphere is very irregular. The main sources of helium are the relatively rare petroliferous regions of the Earth's surface. Despite this fact, the concentration of helium is everywhere constant no matter where it is measured (even over the sea far from land).

Carbon dioxide gives a similar picture. Like helium, its supply to the atmosphere is very irregular. It is produced by the combustion of organic matter, by the vital processes of living organisms, is evolved in large amounts from the bowels of the Earth, particularly during volcanic activity, etc. Despite this, the concentration of carbon dioxide in the free atmosphere varies only very slightly. Its variation is hardly observable, even when comparing samples taken in towns and farming country with samples from areas far from these. Recently (1958), a careful investigation of the carbon-dioxide content of the air in the Antarctic was carried out by the Americans in their base Little America. The results of this investigation showed that even in these barren snow-covered wastes, far from any sources of CO_2, the concentration of this gas was 0.03 % by volume, i. e., precisely the same as at all other points of the globe.

This constancy of composition becomes understandable when we compare the rate of local pollution of the atmosphere with the enormous speed of mixing of the atmosphere as a whole. It should also be remembered that disturbances in the atmospheric equilibrium are quickly reduced by an

* See Table 9.

"internal" correcting mechanism. As an example of such a mechanism we may cite the process already mentioned by us of absorption and evolution of CO_2 by the seas.

The indisputably established fact that the composition of the air near the Earth was constant was the starting point for the investigation of the composition of the upper atmosphere. On the basis of Dalton's law of partial pressures, investigators set themselves the aim of finding the level of gravitational separation of gases, and in search of this they ascended higher and higher in the atmosphere. This search for the level of gravitational separation, and with it for the level of intense atmospheric mixing, did not give positive results up to an altitude of 70–80 km. The atmosphere at these heights was still completely uniform, its composition being identical with that of the air near the Earth. Not until about 100 km was evidence found for the beginning of the separation between gases such as nitrogen and argon.

The high altitude of the level of gravitational separation was evidence for the constant mixing of nearly all the enormous mass of air surrounding the Earth by convection and turbulence, both horizontally and vertically. On this basis, the constancy of the composition of the atmosphere above all points of the Earth's surface is not all surprising: the constant mixing of the mass of atmospheric air does not allow the presence of stable local variations in the atmospheric composition.

In view of this last statement, the well-known fact that the atmosphere does show definite and stable inhomogeneities at altitudes up to about 100 km calls for explanation. We are referring here to the existence of various layers in the atmosphere: in the lower atmosphere the cloud layer, in the upper atmosphere the ozone layer, the ionized *D* layer, the silver cloud layer, etc.

The presence of these various layers in the atmosphere is mainly determined by three conditions*: 1) the presence at the appropriate height in the atmosphere of certain special physical factors responsible for the formation of the layer in question (the presence of the necessary quanta of solar radiation, of a certain concentration of air, temperature changes, etc.), 2) the capacity of certain atoms or molecules penetrating to these heights to assume quickly the properties characteristic of particles of the layer in question (condensation, formation of new compounds, ionization, luminescence, etc.), 3) the capacity of these particles to lose the properties in question quickly on leaving the region in which the special physical factors apply.

It should be added that the speed with which the atmospheric particles gain or lose the relevant properties and the rate of mixing of the atmosphere at a given height should bear a certain relation to one another: the layer will be formed more quickly as the characteristic rate of change of the particles exceeds the characteristic rate of mixing. The "rates" of formation of the various layers in the atmosphere differ; some layers are "fast", and some are "slow", but whatever the rate at which the particles acquire the property in question it is always greater than the rate of mixing in that layer (as long as the layer does exist). As an example of a "fast" layer we may mention the cloud layer found in the troposphere, in a region of

* The dust layer forms something of an exception to this rule, as only the first condition is necessary for it.

intense mixing. Since the condensation of the water vapor and the evaporation of the condensed water occur practically instantaneously at the appropriate temperatures, the cloud layer formed in a region of suitable temperature often has sharply defined upper and lower boundaries despite the mixing of the atmosphere at these heights. The intense vertical currents in this case only aid the formation of the layer, bringing water vapor there from the lower atmosphere.

As an example of a "slow" layer we may cite the ozone layer, situated at an altitude of 15–50 km. This layer, according to the theory of Chapman /136/, should have a specific character, with a sharply defined lower boundary. In fact, the ozone layer does not have such a sharp boundary. This is because the ozone molecules formed in the atmosphere under the influence of solar radiation have quite a long life. The air mixing of these altitudes removes ozone molecules from the regions where they were formed and carries them to lower layers of the atmosphere. In these layers the ozone is not so easily formed because the solar radiation responsible for its formation cannot penetrate there. For this reason, the "slow" ozone layer does not have a sharp lower boundary.

We can also mention many other layers in the zone of atmospheric mixing (the ionized-particle layer, the silver-cloud layer, the layers of fast and slow molecules, i. e., the hot and cold layers, the emission layers, etc.) which are formed and have a stable existence in that part of the atmosphere where mixing occurs because all three of the above-mentioned conditions are satisfied.

If however one or all of these conditions are not fulfilled, then a mixture (or some stable gas) introduced somewhere in the atmosphere will be spread throughout the whole mass of air, since there are no limiting effects to keep it in bounds. Therefore mixing, however slight, eventually evens out the components of the atmosphere.

Considering now the composition of the atmosphere at altitudes above 100 km, we should state that the composition changes in this region. This is not only because above 100 km gravitational separation plays an important role, but mainly because at these altitudes the oxygen molecules dissociate into atoms under the influence of solar radiation of wavelength less than 1750 Å. As a result of this, the composition of the atmosphere in the transition region from 100–200 km shows a new component, atomic oxygen*.

As we have mentioned above, in this altitude range the partial pressure of argon falls appreciably but the presence of the light gases helium and hydrogen in amounts exceeding 10^8 particles per cm^3 (the sensitivity of the measuring equipment, see /115/) could not be detected**.

The neutral composition of the atmosphere has not yet been directly investigated at altitudes much above 200 km, because of the low sensitivity of the radio-frequency mass spectrometer when used for analyzing neutral gas. We can however try to form some conclusions about the composition of neutral particles at high altitudes from the results of investigations of the ionosphere. We shall therefore now have another look at the results of the investigations of the composition of the charge particles in the ionosphere

* The atomic oxygen may react in its turn with nitrogen to give very small amounts of the neutral molecule NO.

** We remind the reader that the concentration of neutral particles at altitudes of 200 km is about 10^{10} particles per cm^3.

and deduce from this material the composition of the neutral atmosphere at high altitudes.

Direct investigations of the chemical composition of the ionosphere using the radio-frequency mass spectrometer can only be carried out at altitudes above 100 km, while the observable ionosphere starts somewhat lower (at about 60 km, D layer). There are therefore hardly any experimental data about the nature of the lowest layers of the ionosphere. Indirect data allow us to draw the conclusion that the main ion in the lower ionosphere is the nitric oxide NO^+; there are also probably considerable quantities of molecular oxygen ions, O_2^+ during the day.

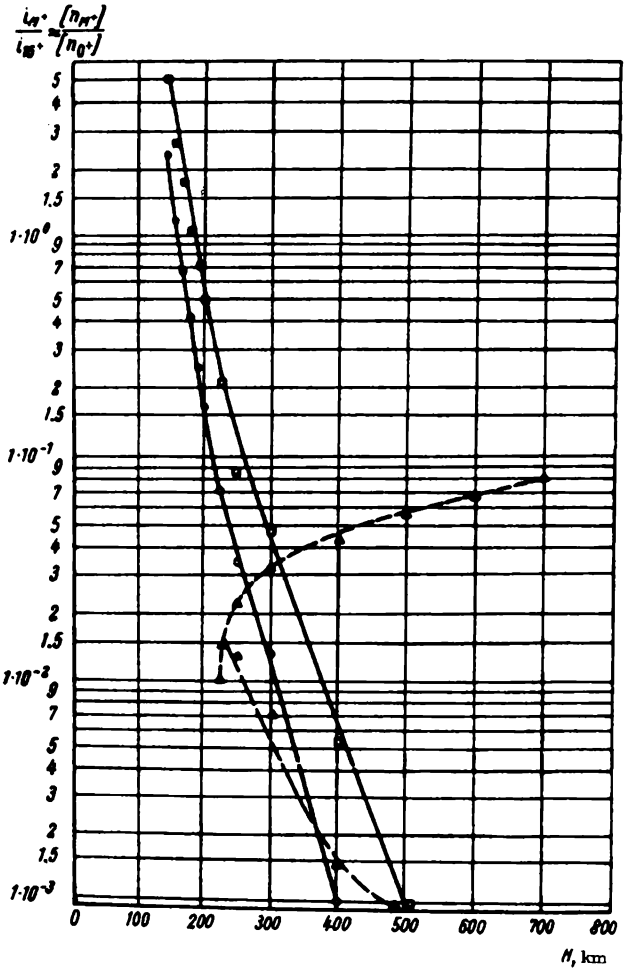

FIGURE 80. Vertical structure of the ionosphere from 150–700 km (according to V. G. Istomin). The concentrations of the various ions are expressed relative to that of the atomic oxygen ion

●,○ – $i_{O_2^+}/i_{O^+} \approx [n_{O_2^+}]/[n_{O^+}]$; ■,□ – $i_{NO^+}/i_{O^+} \approx [n_{NO^+}]/[n_{O^+}]$; ◇ – $i_{N_2^+}/i_{O^+} \approx [n_{N_2^+}]/[n_{O^+}]$; △ – $i_{N^+}/i_{O^+} \approx [n_{N^+}]/[n_{O^+}]$; (●,■ –rocket, August 1958, daytime; ○, □, ◇, △ –Sputnik III, May 1958, daytime).

Between 100 and 150 km the ionosphere is composed of three positive ions: O^+, O_2^+ and NO^+*, here again with NO^+ in the majority.

The composition of the ionosphere changes rapidly between 150 and 250 km: the relative amount of atomic oxygen ions increases rapidly, and this ion predominates at altitudes above 200 km**. Molecular nitrogen ions (in very small amounts) and atomic nitrogen ions are also found here; the relative concentration of the latter has a tendency to increase with height.

The concentration of O_2^+ and N_2^+ ions decreases sharply round about 250 km. The atomic oxygen ion is the principal one here.

Above 250–300 km the relative concentration of atomic nitrogen ions starts to increase; this reaches 7–9 % of the concentration of O^+ at altitudes of 800–900 km.

Figure 80, taken from the work of V. G. Istomin, shows in graphic form the whole picture of the vertical chemical structure of the ionosphere from 150–700 km. When looking at Figure 80, one should not forget that the total amount of ions is very small compared to the neutral particles at high altitudes in the atmosphere. As can be seen from Figure 81, their ratio increases with height, although even at 800–900 km the total ionic concentration is hardly 10 % of the total concentration of gaseous particles***. Therefore, despite the great importance and independent significance of ionic

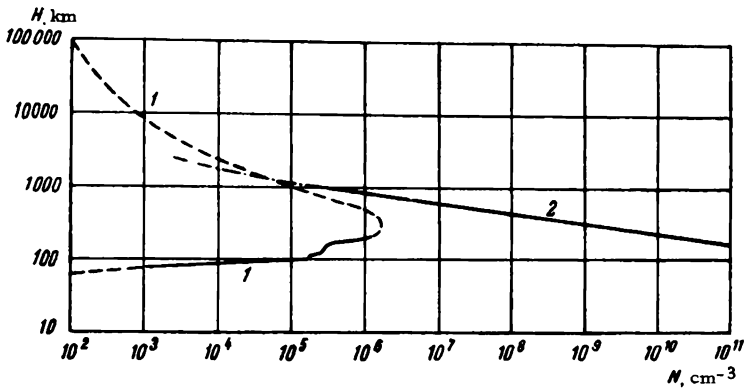

FIGURE 81. Concentration of ions (1) and neutral particles (2) in the atmosphere

particles in the Earth's atmosphere, they must be regarded as a slight "addition" to the atmosphere, merely "tinting" it in this and that shade. Above 1000 km the atmosphere is ionized to a considerable extent; ions appear to be the main component here.

Having considered as far as possible the detailed structure of the ionosphere, let us turn our attention to the composition of the neutral particles which make up the Earth's atmosphere at altitudes exceeding 200–250 km. Here, however, we find ourselves in the region of more or less reasonable assumption.

* Small amounts of the negative ion NO_2^- are also found at these altitudes (see the footnote p. 138).

** The concentration of atomic oxygen ions is approximately equal to that of molecular oxygen ions between 165 and 190 km above the Earth /134/.

*** At an altitude of 300 km the proportion of ions in the atmosphere compared to the total number of particles is about 0.1 %.

What can we say about the composition of the neutral atmospheric particles on the basis of investigations on the chemical composition of the ionosphere?

It seems to us that consideration of the composition of the ionized gases leads to the conclusion that at altitudes of 400–800 km neutral atomic nitrogen is not present to a considerable extent (more than 10 %) in the Earth's atmosphere.

In fact, as shown in /141/, the conditions in the Earth's atmosphere above 200 km are equally favorable for the ionization of atomic oxygen and atomic nitrogen, in other words, the probabilities of atomic oxygen and atomic nitrogen being ionized by the solar radiation are equal. Moreover, it appears that the chances of these atomic ions being lost by transfer of their charge to other ions or by any kind of chemical reaction which may occur in the upper atmosphere are equal*.

All this leads to the conclusion that the ratio of the concentrations of atomic nitrogen ions and atomic oxygen ions should roughly equal the ratio of the concentrations of the neutral atoms. As has been shown, the relative concentration of atomic nitrogen ions at the heights in question is low, so the concentration of neutral nitrogen atoms compared to the concentration of neutral oxygen atoms should also be low.

It may furthermore be concluded on the basis of the investigation of the ionosphere that up to altitudes of 700–800 km, neutral atoms of the light gases hydrogen and helium do not make up an appreciable part of the atmosphere. We have already mentioned that the absence of neutral hydrogen and helium in amounts exceeding 10^8 particles/cm^3 at altitudes of 200 km suggests that the content of these gases is hardly likely to be appreciable even at altitudes of 500–700 km. This is confirmed by the investigation of the helium and hydrogen in the ionosphere /137/. These workers found the upper limit of the concentration of the light gases at about 200 km to be 1000–400 particles/cm^3. Using more sensitive apparatus, Istomin /140/ found an even lower value: 100 particles/cm^3. This low concentration is hardly likely to allow neutral hydrogen to be a significant component of the atmosphere up to 500–700 km. But if the light gases (atomic nitrogen, hydrogen, helium) are not present in large amounts in the upper atmosphere, what kind of neutral particles occur to an appreciable extent at any altitude above 300 km?

Bearing in mind all the conclusions drawn above, and remembering that molecular oxygen will be almost completely dissociated at such high altitudes, we find ourselves left with only two possibilities: either neutral atomic oxygen or neutral molecular nitrogen (the one or the other being mixed with a small amount of atomic nitrogen).

However, the gravitational separation which reigns at these altitudes would make it difficult for large amounts of the relatively heavy nitrogen molecule to be present at such high levels in the atmsophere. We may therefore conclude that the hypothesis that the upper atmosphere, at least up to 1000 km, consists mainly of atomic oxygen (with a little atomic nitrogen /138/) is the most probable one at present.

As regards the even higher layers of the atmosphere, the same should be true of them as of the ionosphere, since most gaseous particles at

* The collision of gaseous particles at altitudes above 500–600 km (in the exosphere) is a relatively rare event, and can (to a first approximation) be neglected when considering the processes leading to the loss of ions.

altitudes exceeding 2000–3000 km should be ionized (see Figure 81). There are reasons to believe /138, 139/ that at these altitudes begins a very extended (up to an altitude of 20,000 or 30,000 km) and very rarified (1000 particles/cm^3) ionosphere, consisting of hydrogen atoms (protons), which gradually changes into the interplanetary gas. The concentration of the latter is at present estimated to be of the order of 100 particles/cm^3 (or even less).

The final conclusions about the composition of the Earth's upper and outer atmosphere must await new experimental data.

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APPENDIX

THE CONCENTRATION OF OZONE IN THE ATMOSPHERE

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Introduction

The main components of the atmosphere, N_2 and O_2, and also A, Kr, etc., are present in constant amounts up to altitudes of about 100 km: the relative concentrations of these components are constant (independent of changes in the meteorological conditions) during significant variations of physical conditions such as pressure, temperature, humidity and the intensity of the solar radiation. Ozone, water vapor and certain other components of the atmosphere do however show considerable variations with changes in the meteorological and physical conditions. Therefore, from studying the variation of the concentrations of ozone and water vapor in the atmosphere we can draw conclusions about atmospheric phenomena which are of great importance in meteorology. The recent extensive soundings of the upper atmosphere, combined with regular ground-level observations, have begun to elucidate the reasons for the seasonal and latitudinal variations in the ozone content, given a clear picture of the circulation of ozone in the lower atmosphere up to 30 km, and allowed concrete relations to be established between the variation of the ozone concentration and a number of meteorological processes.

The main feature of the distribution of ozone in the atmosphere is that its concentration increases appreciably with height, reaching a maximum at about 25 km. This was established soon after the discovery of ozone in the atmosphere by Rayleigh in 1918: he showed that the mean relative concentration of ozone in the atmosphere ($3 \cdot 10^{-7}$) is appreciably greater than its concentration near the Earth's surface ($5 \cdot 10^{-9}$). This is connected with the fact that the absolute concentration of ozone in the stratosphere is about thirty times more than that near the Earth, even though the density of the air in the stratosphere is nearly 100 times less than that at ground level. The existence of an actual ozone layer in the atmosphere was demonstrated by Cabannes and Dufay, who determined the height of this layer from the absorption of solar radiation by ozone as a function of the height of the Sun above the horizon. The absorption by ozone follows a law which differs considerably from that for other components of the atmosphere. This method was worked out by V. A. Ambartsumyan in 1932, was later put into a standard form and is now in general use /11, 16/.

The methods used for investigating ozone, and their results, are extensively reported in the Soviet literature. A survey of the work carried out until the beginning of rocket investigations may be found in the book "Atmospheric Ozone" by Götz /8/. I. A. Prokof'ev's substantial monograph of the same title appeared later /26/, while the more recent books of

A. Kh. Khrgian /38/, S. K. Mitra /22/ and R. M. Goody /10/ also contain detailed accounts of the investigations on ozone. A fairly complete survey of work published before 1955 is given in Sh. A. Bezverkhnii's thesis /4/. The most complete survey, by I. A. Khvostikov /37/, was published quite a long time ago, in 1956, and new results have been obtained since then.

The main problem in the theoretical treatment of ozone is how to explain the vertical distribution of ozone and the existence of a definite ozone layer in the atmosphere. The photochemical theory, despite its successes in other fields, could not explain the seasonal and latitudinal variations of the ozone content and the presence of ozone in the air near the Earth. All these problems were solved when the data about the circulation in the troposphere became available. The main trends in the recent investigations of ozone have therefore been: more precise determinations of the vertical distribution of ozone at all altitudes down to the Earth's surface, the study of the migration of ozone from the stratosphere towards the Earth and its dependence on the latitude and the time of year, and the vertical and horizontal transport of ozone by air currents in the lower atmosphere. Particularly close attention has been paid to the vertical transfer of ozone, its daily and seasonal variations, and its destruction near the Earth's surface. The experimental methods used for this purpose have also been improved. Let us now briefly consider the work carried out recently in this field.

Large-scale plans for investigating ozone were prepared for the IGY. In the period preceding the actual IGY, new equipment was designed, old methods of observation were improved, and preliminary observations were made.

In the Soviet Union, an improved three-channel photoelectric ozonometer OFET-3 with three UV filters /5, 14/ was developed. The OFET-3, like the Dobson spectrophotometer, allows both the overall ozone content of the atmosphere and its variation with height to be determined by measuring the UV radiation from the Sun and the scattered light from the sky. A double quartz monochromator with a photoelectric UV detector was designed for the same purpose at the Moscow State University /20/.

A network of ozone observation stations was set up /14/ in Voekov near Leningrad, Abastumani, Terskol at the foot of Elborus [in the Caucasus Mountains], Alma-Ata, Vladivostok and Dikson Island. One of the main applications was the study of the general circulation of the atmosphere and its connection with the weather: ozone, which has a life of months in the lower atmosphere, was used to indicate the movement of the air masses /9/.

The variation of the overall ozone content and the study of ozone in the lower atmosphere

The determination of the overall ozone content of the atmosphere, i. e., the amount of ozone in a vertical column of cross section 1 cm^2 (usually expressed in mm Hg at NTP), is based on the measurement of the absorption of light by the ozone layer in this column. Not only the Sun but also the Moon and stars are used as light sources, and observations are carried out on the clear or even the cloudy sky at the zenith. In the Sun's spectrum (and those of other heavenly bodies) we observe, apart from the strong absorption band due to ozone in the ultraviolet between 2000 and 3500 Å (the Hartley band and the Huggins bands), the Chappuis band in the visible part

of the spectrum (5000-7000 Å) and the strong infrared bands at 4.75, 9.6 and 14.1 μ. By measuring the absorption in these bands we can determine the overall ozone content of the atmosphere. The methods and apparatus developed for this purpose are described in sufficient detail in /26/. The investigations which we shall now describe are those in which increased accuracy or new results were obtained.

Dobson's method. Dobson's method is based on measurement at the shortest wavelength of the ultraviolet spectrum under investigation, or the determination of the relative intensity at two or more places in the spectrum. The ultraviolet part of the spectrum is convenient because ozone absorbs strongly in this range, and very sensitive ultraviolet photometers are available.

The first correction which had to be made to Dobson's method was occasioned by the recent determination, by Vigroux /157/ and Inn and Tanaka /82/, of new values for the absorption coefficient of ozone in the ultraviolet. These data appeared after Prokof'ev's monograph /26/ was published, but are cited in /16/. Use of the new values of the absorption coefficient led, for example, Stair and Johnston /144/ to change their estimate of the overall ozone content from 2.4 mm Hg to 3.2 mm Hg, while Dunkelman and Scolnik /55/ found 2.43 mm Hg instead of 2.00 mm Hg; the new values are thus 20–30 % higher than the old ones. This far exceeds the experimental error in the determination of the overall ozone content, which is 0.5–2 % with modern measuring methods. Watanabe /168/ gave a detailed summary, in tabular and graph form, of new data on the absorption coefficients of ozone and other components of the atmosphere.

The second correction to Dobson's method concerns the influence of aerosols: scattering by aerosols and by the air itself also cause a certain attenuation of the light, which complicates the absorption measurements. G. P. Gushchin /11/ showed that aerosols may cause up to one third of the attenuation of the light, which is normally all attributed to the ozone. Dunkelman and Scolnik observed a similar attenuation on Mount Lemmon, 2450 m above sea level, while Stair /55/ observed an even greater attenuation. Dunkelman and Scolnik /55/ found that even when the atmospheric transparency is excellent, admixture and pollution cause up to 15 % of the absorption in the spectral region between 3400 and 4650 Å. The light attenuation in the region 4000-5200 Å has been observed by the astronomers V. G. Fesenkov /34/, T. P. Toropova /31/ and M. B. Dolidze /18/. They found relatively rapid, irregular variations in this attenuation in the course of 24 hours, even on days when the atmosphere was exceptionally clear.

According to G. P. Gushchin /11/, the effective radius of the aerosol particles is about 0.11-0.26 μ, and their concentration is about 10^7 per cm^3. About two thirds of the aerosols are concentrated in the first two kilometers of the atmosphere. It should be noted that the optical density of aerosols usually increases towards noon, or on the approach of clouds, which may lead to false conclusions about the diurnal variation of the ozone content of the atmosphere. For example, Craig in his well known monograph /51/ gave data which indicate that the day-to-day variation in the overall ozone content may surpass the fluctuation of the monthly mean value in the course of a year. These changes can hardly be attributed to equally rapid changes in the ozone content: they are related to variations in meteorological conditions which apparently have a greater effect on the aerosol content of

the atmosphere than on its ozone content. This also seems to be the reason why Johansen /88, 89/, Teichert and Warmbt /150, 151/ et al. found a variation in the amount of ozone in the atmosphere with changes in the meteorological conditions, while Rasool /131/ found no such correlation in the same period.

Paetzold and Zschörner /128/ showed that the determination of the ozone content by Dobson's method gave different results for light observed from the Sun and from the zenith; the difference decreases, however, if the spectral temperature of the light is taken into consideration. Rasool's spectrophotometric investigations /130/ showed that selective absorption occurs in Huggin's bands when the sky is overcast. Dobson's method can thus only be used when the sky is clear.

After these general remarks about Dobson's method, we shall proceed to give an account of the various investigations of the ozone content of the atmosphere.

Diurnal and seasonal fluctuations. In the light of the above, one must regard the small fluctuations in the overall ozone content, which are sometimes observed from day to day, with a certain suspicion. The fluctuations of the ozone content in the troposphere as a result of changing meteorological conditions are apparently slight, although, for example, the Föhn winds in the Alps, which cause the rapid vertical displacement of large air masses, are known to cause sudden changes in the ozone content /37, 123/.

It may be concluded that on the whole the overall ozone content of the atmosphere changes little from day to day.

A number of investigations on the seasonal variations of the overall ozone content of the atmosphere have been carried out in recent years, in Alma-Ata /5/, in Voekov and on Elborus /11/, in Japan /78, 93, 108/, Malaya /81/ and other places. These measurements did not produce new results but merely confirmed the by now generally accepted law of the regular seasonal and latitudinal variation of the overall ozone content according to Götz's isopleths, as follows: 1) a sharp increase in the ozone in the early spring, followed by a slow decrease until the beginning of winter, by the same amount in both hemispheres; 2) the seasonal fluctuation in the ozone content at the equator is small (about ± 0.15 mm Hg), but reaches 1 mm Hg at high latitudes; 3) the ozone content reaches a minimum at the end of the autumn, amounting to about 2 mm at the equator but about 2.5 mm at high latitudes; 4) the maximum ozone content is found at a latitude of about 60°.

The latitudinal variation. The measurement of the ozone content in the polar regions during the long polar nights and days is of prime importance for the verification of the photochemical theory. It recently became possible to carry out such measurements. Results obtained in Antarctica /81/ and in the arctic (by Johansen, in Tromsö) /88, 89/ indicate that the ozone content has two maxima, in winter and in late spring.

Douglas, Hertzberg and Rose /54/ measured the overall ozone content at the North Pole by photographing the spectrum of the Moon with a quartz spectrograph placed in an airplane. At the time of the flight, the atmosphere at an altitude of 50 km had not received light from the Sun for about 108 days, and would not do so for another 34 days. The nearest point where the atmosphere at an altitude of 50 km was lit by the Sun was 1200 km from the pole, so that the region of the ozone layer observed was under conditions of deep polar night. The amount of ozone found in this way was the

same as three weeks later in Ottawa. These results do not thus confirm the opinion that there is a deep minimum in the ozone concentration at the pole during the polar winter when the ozone layer is deprived of ultraviolet radiation from the Sun for a long time. However, the aurora polaris and related effects influence the ozone content. Murcray /109/ found that the infrared emission of ozone in the 9.6μ band increased by 18% after a display of the aurora polaris. This indicates either an increase in the ozone content, or an increase in its temperature under the influence of the aurora polaris.

Observations during a solar eclipse. The study of the ozone content during a solar eclipse can give interesting information about the influence of solar radiation on the formation of ozone in the stratosphere /24/. A certain number of such observations have recently been carried out /3, 12, 36, 146/. Kawabata /94/ observed during the eclipse of 19 June 1936 an increase in the ozone content after the first contact (the beginning of the eclipse) and a rapid decrease just before the second contact (the beginning of the total phase of the eclipse)*. Jerlov, Ollson and Schüepp /83/, on the other hand, found during the eclipse of 9 June 1945 (observed at Lövanger) that the ozone content decreased from 3 mm Hg at the start of the eclipse to 2 mm at the end, according to the absorption in the Chappuis band (visible range of the spectrum).

G. P. Gushchin /12/ did not find any change in the ozone content during the eclipse of 30 June 1954 near Leningrad, where the maximum phase of the eclipse was 0.86. Fournier d'Albe and Rasool /66/ found only a small increase in the ozone content. On the other hand, Sh. A. Bezverkhnii, A. L. Osherovich and S. F. Rodionov /3, 4/ found, for the same eclipse and for the eclipse on 25 February 1952, a considerable decrease in the ozone content (from 2.5–0.5 mm Hg) between the first and second contacts, and a sharp increase (to 5.5 mm) during the full phase. The ozone content returned to its equilibrium value $8 \cdot 10^3$ seconds after the full phase. Such large variations in the ozone content in such relatively short spaces of time are hard to understand in the light of our present knowledge. It rather looks as if the above-mentioned observers did not take into account the full complexity of the phenomena involved when interpreting their results.

The determination of the ozone content during an eclipse by measuring the absorption coefficient is complicated by the fact that when the solar disk is covered by the Moon the spectral composition of the remaining solar radiation is changed as a result of the darkening effect at the Moon's edge. This was not taken into account in /4/. This phenomenon has been investigated in detail by B. D. Fomenko /36/, who showed that it is essential to take this edge effect into account. She found that the transparency of the atmosphere for shortwave radiation decreases during the initial stages of an eclipse, but increases again by 5-7% during the period (some tens of minutes) between the phases 0.85. These findings are in agreement with those of Kawataba /94/ mentioned above. The author explained the increase in the transparency before the full phase as being due to a decrease of one third in the ozone content during the eclipse. It is however hard to believe that this can really be the explanation.

Svensson, observing the solar eclipse of 30 June 1954 at Upsala (Sweden), where the maximum phase was 95% /146/, also found an increase in the

* In /26/ and /36/ this was erroneously reported the wrong way round.

ozone content at the maximum phase, i. e., before the second contact, which agrees with /36, 66, 94/. However, it was found that the increase depended on which two wavelengths out of a possible three were used for determining the ozone content. The author showed, like Fomenko, that the apparent increase in the ozone content can easily be explained as being due to the edge effect.

Summarizing, we should mention that we have good reason to believe that the ozone content during an eclipse either does not change at all, or increases slightly in accordance with the theory.

Ozone near the Earth. The total ozone content of a vertical column of the atmosphere depends on the atmospheric circulation. It is therefore interesting to measure the ozone content at various points near the Earth's surface; this might provide a key to the understanding of those important phenomena, the vertical and horizontal transport in the lower stratosphere. The question of the atmospheric circulation is now the main problem of atmospheric physics. Until recently it was not even known whether the ozone was formed near the Earth's surface or transported to the lower atmosphere from the stratosphere, and actually destroyed near the Earth. This could only be ascertained after many observations of the ozone concentration near the Earth had been made.

Routine measurements of the ozone concentration near the Earth are usually carried out by chemical methods (see /10, 22, 26/). These methods are limited to local measurements, and their results should be regarded with some caution. For example, Rasool and Vassy /132/ found that the chemical method which they used gave lower results than the optical method when it was windy. The chemical method has recently been improved /147/ so as to prevent atmospheric NO_2 from having any effect on the determination of the ozone concentration. Chemical analysis is used in automatic weather stations (Regener /47, 81, 137/).

Successful use has recently been made of an optical method involving the measurement of the absorption of ultraviolet /42, 29/ or infrared radiation /148/ from a source several kilometers (up to 20 km) away. This method allows the mean concentration over a relatively large area of the Earth's surface to be measured, so that the results are independent of local variations in the ozone concentration.

The results of the many measurements of the ozone concentration near the Earth's surface may be summarized as follows: the average seasonal variations follow those of the overall ozone content of the atmosphere /41, 82, 151, 167/, i. e., there is a maximum in the spring and a minimum in the autumn. It should however be realized that the abnormal local meteorological conditions, e. g., in Alma-Ata /1, 2/ and the Alps /123/, may distort the seasonal alterations. Peculiar changes are also observed in Antarctica /81/: the concentration of ozone near the Earth's surface increases suddenly at the beginning of the winter (April), when the polar night sets in, and slowly decreases from September-February.

The daily variation of the ozone concentration is much more complicated. A minimum is generally found in the morning, and the concentration of ozone near the Earth is on the average less at night than in the day, by a factor of 2 to 10 /27, 41, 45, 78, 149, 151/. This daily fluctuation is found to be greater in valley regions than on mountains, because of the variation in the vertical mixing by turbulence in the lower atmosphere, which is less at night when a stable stratification of the lower atmosphere sets in.

Sometimes the ozone concentration at night is actually found to be more than in the day /167/. In Malaya the maximum ozone concentration is found in the morning, with the minimum at noon. This is connected with the peculiar local circulation of the air /81/. The ascending and descending currents of air are here controlled by the heating and cooling of the rocks: in the morning, the air currents descending from regions with a higher ozone concentration give rise to the maximum in the concentration at this period of the day.

The ozone concentration at different places on the Earth's surface differs*; the mean concentration at a given spot may lie between 5 and 25 γ/m^3. Even lower concentrations, down to 10^{-4} cm/km ≈ 2 γ/m^3 or less, are sometimes found in cases of temperature inversions at heights of 400–500 m /131, 149/, which prevents the vertical mixing of the air masses. According to measurements made by Kauer, Regener and Ehmert, the concentration of ozone in sea air is greater than 25–60 γ/m^3 (which corresponds to the concentration on a mountain top) and varies less in the course of the day. Jessel /84/ relates this to the high purity of sea air, which does not contain oxidizing agents, and the intense vertical turbulence in the first few tens of meters of air above the surface of the sea both by day and by night. An increase in the ozone concentration is often found in the presence of a sea breeze, while a breeze from inland can cause a decrease in the ozone concentration in coastal regions. If these breezes occur in a regular pattern, they will determine the daily variation of the ozone concentration /167/.

Transport of ozone from the stratosphere to the troposphere. In order to find out whether ozone is formed in the lower atmosphere or if it descends from the stratosphere, the ozone concentration was measured at various heights near the Earth. A. and H. Ehmert /59/ measured the concentration at heights of 1.4 and 20 m, while Teichert /149/ made 222 observations by means of chemical analysis in 1953-1954, at ground level and on top of a mast 80 m high. Regener /136, 137/ carried out systematic observations at four heights: 0.4, 1.6, 6.25 and 12.5 m. The ozone concentrations at all heights were found to undergo simultaneous parallel changes. This showed /137/ that the breakdown of the ozone is caused by solid and liquid aerosols present in the atmosphere at all heights, and not by contact with the earth or with vegetation, as was previously thought. It was found that the ozone concentration increases systematically with increasing height, which indicates that it reaches the Earth from the upper atmosphere. The idea that the ozone in the lower atmosphere comes from the stratosphere was put forward in the 40's by Regener and co-workers /90, 118/.

Starting from the fact that practically all the ozone in the 10 m layer of air near the Earth is destroyed during the night, Paetzold /122/ estimated that on the average about $4 \cdot 10^{10}$ molecules O_3/cm^2 sec disappear in the course of the day. This means that a current of $4 \cdot 10^{10}$ molecules O_3/cm^2 sec must reach the Earth from the upper atmosphere, which is in agreement with the data on the turbulent mixing and diffusion of ozone in air. This also explains why near the equator, where the atmospheric mixing is known to be more intense, the overall ozone concentration is less than at higher latitudes, although the stronger solar radiation above the equator means that

* Different authors give their results for the ozone concentration in different units, which at normal temperature and pressure are related as follows: 10^{-8} relative units (by volume) = 10^{-3} cm/km = 21.4 γ/m^3 = $= 2.14 \cdot 10^{-5}$ g/m^3 = $2.7 \cdot 10^{11}$ molecules/cm^3.

more ozone is formed there in the course of the year. Paetzold found /120/ that according to the photochemical theory $5 \cdot 10^{10}$ molecules O_3/cm^2 sec should be formed on the average in the atmosphere. This agrees well with the estimate of the breakdown of ozone near the Earth. This thus demonstrates the existence of a continuous ozone-oxygen cycle in the Earth's atmosphere /127/: the oxygen rising to the upper atmosphere is turned into ozone. This is carried back to the Earth and there transformed into molecular oxygen.

Regener recently /136, 137/ made a new estimate of the ozone transport on the basis of more extensive data, and arrived at a value of 0.9-$2.5 \cdot 10^{11}$ molecules O_3/cm^2 sec. This rate is enough for the transport of all the stratospheric ozone to the Earth in the course of a year, i. e., for the annual renewal of all the ozone in the atmosphere. The annual variation of the overall ozone content suggests that this renewal can in fact occur more frequently.

Although in general ozone is transported to the Earth from the upper atmosphere (the stratosphere), under certain conditions it may be formed at the Earth's surface. An appreciable increase in the ozone concentration is found after thunderstorms /29, 30, 42, 156/. As Vassy /154/ showed, the zone concentration increases not only in summer during thunderstorms, but also in winter. He therefore concluded that this increase is not due to the lightning but to the silent electrical discharge. Laboratory work confirmed that lightning gives rise not to ozone but mainly to oxides of nitrogen.

Investigation of the chemical composition of the air in ten American cities /50/ showed that the concentration of oxidizing agents, including ozone, was usually low and inversely proportional to the concentration of SO_2. However, in some industrial regions large amounts of ozone can be formed /67/, and carried long distances by the wind. For example, /166/ the air in Beltsville contained considerable amounts of ozone carried by the wind from Washington, where it was probably formed in the exhaust gases of automobiles. In Los Angeles /67/ the ozone concentration sometimes rises to 0.05 mm/km and more, i. e., as much as in the stratosphere. Ranzetti /138/ measured the daily variations in the relative concentration of ozone and other oxidizing agents. He found that the concentration varied from 10^{-8} and less to 10^{-6}. Frenkiel /67/ pointed out the possibility of ozone formation in the atmosphere by photochemical reactions in the presence of low concentrations of NO_2 and hydrocarbons.

Balloon investigations. It is known that the relative and absolute concentration of ozone in the troposphere increases with height. This followed from the measurements of the distribution of ozone with height in the atmosphere up to 14 km, carried out in the Soviet Union in 1937 by M. A. Konstantinova-Shlezinger, using fluorescence analysis for the samples. The same result was given by the balloon investigations of E. and V. Regener, who measured the ozone distribution with height by photographing the Sun's spectrum in 1934 /134/ and 1947, and also by the photoelectric measurements of Koblents and Stair in 1935 and 1938-1940 /51/. Paetzold /121, 122/ carried out 17 successful experiments using balloons and radiosondes. Apart from his main finding that the relative ozone concentration increases with height (his results are given below), he found that sometimes, mainly in the spring, there is a secondary maximum at altitudes of 10-15 km and even a tertiary one at 7 km. A similar finding had been made earlier by

Götz, Karondikar and Ramanatan /26/ by means of the inversion effect, but with insufficient accuracy. Paetzold explained these extra maxima as being due to the transport of ozone from the polar regions, which are rich in ozone /117/.

Airplane measurements. The well-known investigations of the ozone concentration using airplanes are of interest. In 1949 the results were published of the airplane measurements carried out by Ehmert in August 1942 up to an altitude of 9 km /26, 59/. These data do not confirm the increase in the ozone concentration with height, but show a maximum at about 4 km. Regener and Kay found in 1953 that the relative ozone concentration in the tropopause over England (at an altitude of 12 km) was 5.5 times that near the Earth, while Bruver's measurements over Norway with improved equipment showed higher concentrations of ozone but less variation with height /90/. Kay /21/ gives a summary of 15 airplane investigations using chemical methods. The measurements of 1952-1953 were carried out up to altitudes of 12 km, where the overall ozone concentration in a column of air of cross section 1 cm^2 was as much as 8.5 %. On the average he found a systematic increase of both the relative and the absolute ozone concentration with height, with however variations on certain days.

G. P. Gushchin /15/ carried out 11 airplane investigations in 1956-1957, using a special optical ozonometer. The advantage of airplane measurements is that it is possible to collect a large amount of data during the flight, from which the longitudinal and latitudinal distribution of the ozone can be determined. The effect of aerosols and the scattering of light were taken into account when calculating the ozone concentration. He found that the maximum deviation of the ozone concentration from the mean value during a single flight was 11 %, which shows that the spatial variations in the ozone concentration are slight.

Investigations on the vertical distribution of ozone at high altitudes

The lunar-eclipse method. The Soviet Academician V. G. Fesenkov worked out /32, 33/ and developed /35/ a method for investigating the distribution of ozone in the atmosphere by photometry of lunar eclipses in the visible region of the spectrum, which includes the Chappuis ozone-absorption bands. He calculated tables for the determination of the vertical distribution of ozone from the measured gradient of the luminous intensity in the neighborhood of the edge of the Earth's shadow on the Moon's surface. He also showed that we must not neglect the angular dimensions of the Sun /35/. This method was used by Paetzold in Germany /115, 119/ and Vigroux /158/ in France. Using this method it is possible to determine the geographical distribution of ozone by almost simultaneous measurement of the ozone distribution with height at various points on the Earth's surface, situated at different latitudes and longitudes.

From the data obtained at different latitudes by these means the effect was determined on the ozone of such widely different factors as the tendency to photochemical equilibrium and the redistribution as a result of air movements /117/.

Rocket investigations. The vertical distribution of ozone in the atmosphere can be measured accurately by photographing, at various altitudes

above the Earth, the ultraviolet spectrum of the Sun in the region of the strong ozone absorption band at 2100-3200 Å (the Hartley band) using spectrographs mounted in rockets /7/ and balloons /27/.

Using the rocket "FAU-2", launched on 14 June 1949 when the Sun was just on the horizon, the ozone concentration up to the record altitude of 70 km was determined /28, 86/. In the rocket experiment of 10 October 1946, the ozone concentration was measured up to an altitude of 67 km /85/. It was possible to measure up to such high altitudes because the path followed by the Sun's rays was 30 times longer with the Sun on the horizon than with the Sun at the zenith. This gave the method its maximum sensitivity. V. N. Pokrovskii /25/ gave the formulas for calculating the ozone concentration from the measured intensities of the ultraviolet solar radiation at different altitudes. Apart from photographing the spectra, the ultraviolet light was recorded at various selected parts of the spectrum using a photomultiplier /152/ and photon counters /17, 49/. This method has the advantage that it can also be used in a satellite, as suggested by Singer /141, 142/.

A survey of the results from the determination of the ozone concentration using rockets is given in /17, 140/. Data on the concentration of ozone (number of molecules of O_3 per cm^3) above 30 km obtained using rockets are given in Table 1, rows 1–5.

The difference between the data for altitudes above 30 km on different days must be considered as real, since it exceeds the experimental error and is confirmed by data obtained by other methods. This variation is connected with the vertical movement in the atmosphere at these altitudes /17/. This movement can only lead to a variation in the ozone concentration if the relative ozone concentration in the air varies with height. The data given show that after the maximum, which generally occurs at altitudes of 25–30 km and sometimes at 45 km /152/, the relative ozone concentration gradually decreases with height, proportional to the density of the atmosphere. Thus, ozone is distributed in the atmosphere not only according to the absolute concentration but also according to the concentration relative to the density of the air. This distribution is in the form of a belt with a maximum at altitudes of 20–40 km (depending on the time of year and the latitude), with a gradual decrease in the concentration both towards the Earth and towards the outer limits of the atmosphere. This distribution of ozone was predicted and explained by the photochemical theory (see below).

Balloon investigations. In the USA, the absorption spectrum of ozone at various altitudes was determined photographically on a few occasions only with the aid of the above-mentioned rocket "UAF-2". A more widely used method, using balloons, was suggested in 1934 by E. and V. Kh. Regener /134/, and later used in Germany by Kulcke and Paetzold /98, 99/ and in France by Rasool and Vassy /133/. This method is considerably cheaper than the rocket method. Therefore, although the maximum altitude of 38 km /121, 122/ or even 44 km /126/ reached by radio sondes is considerably less than that reached by rockets, considerably wider and more complete data on the distribution of ozone near the region of maximum concentration have been obtained with balloons. Radio sondes can be used for photoelectric recording of the ultraviolet light. However, this gives somewhat less accurate results than photographing the spectra. The results obtained with balloons are summarized in /27, 121, 129/, and data obtained for altitudes above 30 km are given in Table 1.

TABLE 1

No.	Method		Date	Ozone concentration at various heights, molecules/cm^3							
				30 km	35 km	40 km	45 km	50 km	60 km	67 km	70 km
1	Rockets /17/	Photographic	10 October 1941	$20 \cdot 10^{11}$	$3 \cdot 10^{11}$	$1 \cdot 10^{11}$					
2	Rockets /17/	Photographic	2 April 1949	12	2	–					
3	Rockets /17/	Photographic	14 June 1949	25	14	4.6	$2.1 \cdot 10^{11}$	$5.5 \cdot 10^{10}$	$7.3 \cdot 10^{9}$	$2 \cdot 10^{9}$	$6.0 \cdot 10^{8}$
4	Rockets /17/	Photoelectric	25 January 1950	8.8	6	3.7	2.2	4.6	6.0	1	
5	Rockets /17/	Photon counter	5 May 1951	–	14	6.0					
6	Sondes /121/		1955	10–27	~10						
7	Inversion effect /51, 165/		1950	13–25	8–18	3–5	0.8–2.5	5			
			1959	21	15	7	2.5	7			
8	Lunar eclipses /27/		1957	6–30	2–10	1–2					

TABLE 2

h, km	$J_2 n_2$	$k_{12} n_2 n$	$2k_{31} n$	$k_{13} n_3$	$k_{23} n_2 n_3$	$2k_{33} n_3^2$	$2J_2 n_2 \cdot 10^{-6}$	$\frac{J_2 n_2}{2J_3 n_3}$	n_3 day (observed)	n_3 night (theoretical)	n_2
70	$5.3 \cdot 10^{6}$	$5.35 \cdot 10^{-5}$	$7.2 \cdot 10^{-17}$	$4.45 \cdot 10^{-8}$	$1.2 \cdot 10^{-12}$	$1.8 \cdot 10^{-15}$	1.3	4.1	$6.0 \cdot 10^{8}$	$8 \cdot 10^{11}$	$1.2 \cdot 10^{11}$
60	$6.35 \cdot 10^{7}$				$2 \cdot 10^{-5}$		2.7	23	$7.3 \cdot 10^{9}$		
50	$4.5 \cdot 10^{8}$	$8.0 \cdot 10^{-3}$	$9.2 \cdot 10^{-16}$	$1.35 \cdot 10^{-4}$	$1.26 \cdot 10^{-2}$	$8.4 \cdot 10^{-8}$	11	41	$5.5 \cdot 10^{10}$		$5.6 \cdot 10^{10}$
40	$2.1 \cdot 10^{9}$	$1.07 \cdot 10^{-1}$	$3.4 \cdot 10^{-15}$	$6.1 \cdot 10^{-4}$	$7.8 \cdot 10^{-3}$	$4.6 \cdot 10^{-5}$	2.7	770	$4.6 \cdot 10^{11}$		
30	$4.0 \cdot 10^{9}$	$2.4 \cdot 10$	$1.5 \cdot 10^{-14}$	$1.0 \cdot 10^{-3}$	$5.6 \cdot 10^{-5}$	$3.1 \cdot 10^{-6}$	3.4	1180	$2.5 \cdot 10^{12}$		$6.2 \cdot 10^{8}$

Seasonal variation of ozone at different altitudes. Below 30 km the ozone concentration undergoes considerable changes in relatively short periods of time. During these changes secondary and sometimes even tertiary maxima are found in the vertical distribution /37/. Paetzold /121, 122/ found on the basis of the results obtained during 17 successful balloon ascents, together with the data of other authors, that at different altitudes there is a seasonal variation in the ozone content. At altitudes above 30 km the ozone concentration is maximum in the summer and minimum in the winter, as predicted by the photochemical theory. However, at altitudes below 20 km, where the main mass of ozone is concentrated, the maximum ozone concentration is found in the spring, which is also the case for the overall ozone concentration. In the region between 20 and 25 km, the maximum shifts from spring to winter, and the minimum from autumn to summer, while exactly the opposite variation is found at altitudes around 30 km. The summer minimum here is apparently connected with the transport of ozone downwards by turbulent currents, which are maximum in the summer. The seasonal variation in the intermediate region from 25–30 km has not been determined. Recently, all these results were confirmed by Epstein, Osterberg and Adel /63/, who carried out 124 measurements of the vertical ozone distribution by the "Vodaro" method (see below). The 1000 curves obtained by Dütsch /57/ over a period of three years by the inversion method also confirm these conclusions. All these data are also in agreement with Regener's theory /135/ modified by Paetzold /117, 118, 120, 126/ about the vertical transport of ozone by turbulent mixing (which is maximum in the summer when the solar radiation increases) from the stratosphere to the regions below 25 km, where according to the photochemical theory there should be no ozone at all.

Inversion method. Although the investigation of the ozone concentration near the Earth and of the overall ozone concentration solve some problems connected with ozone, the study of the vertical distribution of ozone gives more valuable results. As we have seen, land-based methods continue to play a large part in this study.

One of the most useful of these methods is that based on the inversion effect ("Umkehr effect"). As is known, this method consists in measuring the intensity of the light reflected from the sky at two wavelengths. When the Sun approaches the horizon, this ratio passes through a minimum and then increases again, owing to the way in which the ozone concentration varies with height. We shall now consider this method in some detail. The first determinations of the height of the ozone layer, based on measurement of the absorption of the direct rays from the Sun when it was nearing the horizon, gave results which were much too high. At the same time the correct vertical distribution of ozone was determined for the first time simultaneously by the Regeners /134/ using a spectrograph carried by a balloon and by Götz, Meetham and Dobson /76/ using the inversion effect. The two methods gave concordant results. Later simultaneous measurements of the ozone distribution above New Mexico using rockets and the inversion method also gave excellent agreement, except that the inversion effect gave values which were too high at altitudes of 35–50 km /17/. Apart from this, the inversion method has a number of serious disadvantages, and cannot give a completely unambiguous and detailed picture of the vertical distribution of ozone. In 1933 K. Pekeris discussed with Götz the whole

basis on which this effect is explained. S. F. Rodionov related the explanation of the inversion effect to the anomalous transparency produced by the atmospheric aerosols. This discussion is reproduced in sufficient detail in /26, 37/. A further argument against using the inversion effect for determining the vertical ozone distribution has since been given by Sh. A. Bezverkhnii /1, 4/. He showed that the inversion effect does not always occur, as it should if it is an inseparable property of the specific distribution of ozone with height in the atmosphere. Larsen /101/ also showed that the form of the inversion effect changed appreciably from day to day, especially when the Sun was just above the horizon, and that this was not due to an actual change in the vertical distribution of ozone but only reflected the limitations of the inversion method. Nevertheless, the inversion effect continues to be used /20, 39/, and even modified. Walton /39/ calculated the effect of secondary scattering, and claimed to have observed the effect not only at the zenith but also in other parts of the sky /163, 164/. Dütsch (/39/, p. 142, /57, 58/) gave an example of how to calculate the ozone distribution on a high-speed computer. Mahmoudian /102/ suggested using the absorption by ozone in the visible range of the spectrum (Chappuis bands) for observing the inversion effect.

G. P. Gushchin /13/ recently strongly criticized the opponents of the use of the inversion effect. He showed that Pekeris had used physically unjustifiable assumptions about the form of the distribution of ozone with height in his objections. Gushchin also calculated the influence of aerosols on the inversion effect, and showed that this influence is not enough to change the basic features of the effect. The discussion as to the justification for using the inversion effect may thus be regarded as closed, and the method may be assumed to be both reliable and useful.

Walton /165/ recently gave detailed tables and nomograms for the rapid calculation of the vertical distribution of ozone from measurements of the inversion effect. He estimated the effect on the accuracy of the results of neglecting the secondary scattering. The Dobson spectrophotometer allows the logarithm of the ratio of the intensity of the light at the two chosen wavelengths to be determined with an accuracy of ± 0.25, from which it may be concluded that the accuracy of determining the overall ozone content is about 20 %.

Strong's method. A method proposed by Strong /145/ in 1941 has recently been developed. This method does not allow the vertical distribution to be determined, but merely gives the mean or effective height of the ozone layer. The method compares the values of the absorption in the ultraviolet, which does not depend on the pressure of the ozone, and in the infrared (the 9.6μ band), which does. This comparison gives a value for the effective pressure of the ozone and also of the effective height of the layer. Watanabe showed in 1943 that the effective height varied from 20.4–24.7 km.

A very detailed study of the infrared absorption spectrum of ozone from $2.8-23.7\mu$ was carried out by Migeotte, Neven and Swensson /105/. They recorded 527 ozone lines and investigated the fine structure of the 9.6μ band in detail. The intensity and frequency of the lines of the rotation spectrum of ozone, and also the absorption by ozone molecules in the infrared, have recently been calculated by Gora /75/. The preliminary publications by Goody and Walshaw /71, 73, 113, 161/ describe a method for determining the effective height of the ozone layer and some results obtained with it; the later publication /162/ gave more accurate results. For

the recording of the infrared solar spectrum in the 9.6μ band they used a monochromator which completely excluded all scattered light, as indicated by the absence of any residual lines in the 6.3 and 13.5μ water bands. They made 202 observations of this spectrum in 1952 and 370 in 1953-54. Calibration curves of the absorption for various pressures were determined on the basis of laboratory measurements. The effective height of the layer as determined from the mean pressure p, where

$$\bar{p} = \frac{\int_{p_1}^{p_2} p\rho dh}{\int_{p_1}^{p_2} \rho dh}, \qquad (1)$$

varied between 16.0 and 20.8 km. This height is considerably less than that of the maximum of the layer, but it corresponds to the effective height calculated from direct measurements using radio sondes /162, 125/. The accuracy of the effective-height determination was to within 0.9 km. It was shown that the effective height is determined not only (and perhaps not so much) by the distribution of ozone in the stratosphere, but also by the distribution in the lower 10 km of the atmosphere. The effective height of the ozone layer was found to vary by about 3.4 km in the course of the year, with a minimum in the summer months (June-August in 1952 and May-June in 1953).

Similar work has been carried out by the Americans Epstein, Osterberg and Adel /60, 61, 62/. They called their method the "Vodaro" method (vertical ozone distribution from absorption and radiation by ozone). They carried out 124 measurements of the effective height of the ozone layer, which varied between 15 and 24 km. In 1955 the minimum height was found in March-April, which does not agree with the results of the previous authors.

Goody and Roach /72/ and Epstein, Osterberg and Adel /60, 61, 62/ suggested measuring the infrared emission of ozone in the 9.6μ band as well as its absorption. This can be regarded as a very important addition to and development of Strong's method. From the measurement of three parameters of the ozone layer, the overall ozone concentration (from the absorption in the ultraviolet), the effective pressure (from the absorption in the infrared) and the effective height (from the mean emission temperature), it is possible to estimate more accurately the character of the vertical distribution of ozone than was originally possible with Strong's method. A sample calculation is given in /72/. The ozone layer is divided into three zones, in each of which the ozone distribution is given by a characteristic expression, the parameters of which are determined from the radiosonde measurements. The problem is now to determine these parameters on the basis of the three above-mentioned measurements. According to Goody and Roach /74/, the ozone content at altitudes characterized by pressures of 1000 and 300 millibar (0 and 13 km) is 0.03 and 0.13 mm respectively. They also found the overall concentration of ozone in the troposphere to depend on the time of year and the effect of advection.

The method suggested by Goody and Roach, and also by Epstein, Osterberg and Adel, has also been used with success by Vigroux /159, 160/. When determining the emission of ozone in the 9.6μ band, Vigroux took into account the effect of the gaseous hydrocarbon band at 10.4μ, and also the absorption by water vapor in this region of the spectrum. He gave a

detailed method of calculating, and introduced some new assumptions about the distribution of ozone in the troposphere. The curves calculated by him for the vertical distribution of ozone according to his four series of measurements agree well with the results of the balloon measurements.

Photochemical theory

The first attempts to explain the existence of ozone in the atmosphere and its distribution with height were made in 1930 by Chapman, and also by Wolf. A cycle of photochemical reactions completely explaining the behavior of ozone was given by Chapman. The quantitative investigation of the ozone content and its variations involves a series of difficulties. These problems were tackled by Wolf and Dimming, Schreier, Craig, Bates and Nicolet, Johnson, Purcell, Tousey and Watanabe, Dütsch and Paetzold. The work of these authors is sufficiently well described in the articles mentioned at the beginning of this chapter.

The basic equations describing the rates of formation and destruction of oxygen and ozone are known to have the form

$$\frac{dn_1}{dt} = J_3 n_3 - n_1 (k_{12} n_2 n + k_{13} n_3 + 2k_{11} n_1 n) + 2J_2 n_2, \tag{2}$$

$$\frac{dn_3}{dt} = -J_3 n_3 + n_1 (k_{12} n_2 n - k_{13} n_3) - k_{23} n_2 n_3 - 2k_{33} n_3^2, \tag{3}$$

where n_1, n_2, n_3 and n are the concentrations of atomic oxygen, molecular oxygen, ozone, and the atmosphere as a whole, respectively; J_2 and J_3 are the photodissociation constants of oxygen and ozone under the influence of solar radiation, and the various k_{ij}'s are rate constants for the reactions between i and j (i. e., molecules containing i and j atoms of oxygen respectively). The values of the various terms of equations (2) and (3) as calculated for different heights are given in Table 2, it being assumed that $n_2 = \frac{1}{5} n$, and n_3 being taken from the rocket data of Table 1.

The theory of the ozone layer should explain the distribution of ozone above and below the region of maximum concentration. The following conclusions can be drawn from Table 2. At all altitudes above 30 km, $2k_{33} n_3^2 \ll k_{23} n_2 n_3$, while $k_{23} n_2 n_3$ and $2J_2 n_2 \ll J_3 n_3$, and $k_{13} n_1 n_3$ and $k_{11} n_1^2 n \ll k_{12} n_1 n_2 n$. It is clear from these inequalities that, among other things, the effect of the ultraviolet radiation from the Sun at these altitudes is not to produce ozone but to destroy it. At these altitudes equations (2) and (3) both reduce to

$$\frac{d(n_3 + n_1)}{dt} = 0 \quad \text{or} \quad J_3 n_3 = k_{12} n_1 n_2 n. \tag{4}$$

This equation means that above 30 km the main mechanism for the formation of ozone is the reaction $O + O_2 + M \rightarrow O_3 + M$, and the main process balancing this is the photodissociation of ozone under the influence of sunlight, $O_3 + h\gamma - O_2 + O$. The total concentration $n_1 + n_3$ should remain constant during the course of the day. It is important to stress here that the photodissociation of ozone is the most effective of the known reactions for the formation of atmospheric oxygen during the daytime up to altitudes of 80 km. Now it is generally assumed that the main source of atomic oxygen is the photodissociation of molecular oxygen under the influence of the solar ultraviolet radiation in the Schumann-Runge continuum. Bates and

Nicolet /44/ considered this true for the region of the atmosphere above 80 km, and their view has recently been verified by Barth and Kaplan /43/. According to later rocket investigations /100/ the dissociation of oxygen increases rapidly in this region. At altitudes of 30-80 km the dissociation of molecular oxygen under the influence of the solar ultraviolet radiation is much less than that of ozone, as may be seen from Table 2: even at 70 km, the latter is four times the former. Thus, unless there is an effective mechanism for the formation of molecular oxygen, as yet unknown to us, at altitudes of 30-80 km, its concentration should be subject to considerable daily variations, as has been observed by Bates and Nicolet /44/. It would be interesting to check this by means of rocket experiments.

Equation (4) may be used to determine the value of n_1 for daytime, as the concentrations n_2, n_3 and n, and the constants j_3 and k_{12}, are known. The results of these calculations are given in the last column of Table 2; they agree well with Mitra's estimates /107/. Normally, when considering the photochemistry of ozone, the concentration of atomic oxygen is calculated from the equation

$$J_2 n_2 = k_{11} n_1^2 n + k_{13} n_1 n_3, \qquad (5)$$

which can be obtained by subtracting equation (3) from equation (2) and neglecting the small terms $2k_{33}n_3^2$ and $k_{23}n_2n_3$. However, equation (5) does not take proper account of such physical processes as the dissociation of molecular oxygen under the influence of solar ultraviolet radiation and the recombination of atomic oxygen by the reactions $O + O + M \rightarrow O_2 + M$ and $O + O_3 \rightarrow 2O_2$, which are not predominating and do not form a closed cycle.

Thanks to the effectiveness of the processes of ozone photodissociation and of ozone formation by the reaction $O + O_2 + M \rightarrow O_3^* + M$ during the day, the main mass of atomic oxygen in the atmosphere above 30 km is transformed into ozone during the night, while during the day the reverse reaction occurs, from ozone to oxygen /96/. These two reactions do not effect the overall concentration of oxygen and ozone, $n_1 + n_3$, in the region of the atmosphere above 30 km. However, the overall concentration increases by a certain amount every day as a result of the dissociation of molecular oxygen under the influence of the solar radiation. As may be seen from Table 2, this daily increase in $n_1 + n_3$ cannot be compensated by the formation of O_2 by the reactions $O + O + M = O_2 + M$ and $O + O_3 = 2O_2$ or any other reactions, because of their low probability. Thus a steady increase in the concentration $n_1 + n_3$ should be observed. That this is not observed is a result of the fact that turbulent mixing causes a continuous flow of n_3 from the upper to the lower atmosphere. An average daily equilibrium should thus be established between the photodissociation of oxygen and the transport of ozone to the Earth's surface and its destruction there. As has already been mentioned, Paetzold's calculations /127/ did indeed confirm the equality of the rates of these two processes. It follows from this that the seasonal variation in the overall ozone concentration in the atmosphere is determined not only by the fact that the photodissociation of oxygen increases in the summer, but also by the annual variation in the rate of mixing, which apparently reaches a maximum towards the autumn, and gives rise to a minimum in the overall concentration of ozone. The establishment of the fact that ozone is transported to the Earth and applying this fact to the hypothesis of the ozone-oxygen cycle systematized our knowledge of the seasonal changes in the ozone layer. The fact that the concentration

of ozone is nearly doubled in the winter (somewhat less than a third of the year in practice), despite the decrease in solar radiation during this period, shows that it is probable that the ozone is renewed more than once a year.

Although the main development of the photochemical theory was complete by 1950-1953, certain points of the theory have been refined since then. Craig and Ohring /52/ calculated the photochemical equilibrium at altitudes of 45-60 km with the Sun at various heights above the horizon and at various temperatures in the range 200-300°K. Similar calculations were carried out by Horiuchi /77/, who used new data on the spectral distribution of the solar radiation in the ultraviolet /87/ (given in /19/, where unfortunately impermissible interpolation is used, and in /16/). The concentration of n_3 obtained by him for an altitude of 40 km is an order of magnitude higher than the experimental value. The author assumes that this is due to the use of too high absorption coefficients for ozone. It is also possible that the use of equation (5) is also a contributing factor.

Nicolet /111/ stressed the importance of considering the formation of OH from ozone by the reaction $H + O_3 \rightarrow OH^* + O_2$ /44/ when calculating n_3. McKinley, Garvin and Boudart /104/ investigated this reaction under laboratory conditions. They found the reaction to proceed at a good rate, giving excited OH* radicals which later lost their energy in the form of radiation. This reaction is very important in explaining the luminescence of hydroxyl in the atmosphere, although V. I. Krassovskii /95/ considers the reaction $O_2 + H \rightarrow OH^* + O$ more likely.

Nicolet /110, 112/ found that above 50 km the equilibrium concentration of ozone at night is two-four orders of magnitude (100-10,000 times) greater than in the daytime. This is easily explained. It follows from equation (3) that at night, when $J_3 = 0$, the main process removing ozone is the reaction $O + O_3 \rightarrow 2O_2$, which balances the ozone-forming reaction $O + O_2 + M \rightarrow O_3 + M$. We now find the following expression for the calculation of n_3:

$$k_{12} n_1 n_2 n = k_{13} n_1 n_3 \tag{6}$$

or

$$n_3 = \frac{k_{12}}{k_{13}} n_2 n.$$

For example, at $h = 70$ km,

$$n_3 = 10^{-18} \frac{4 \cdot 10^{20}}{5} = 8 \cdot 10^{11},$$

which is three orders of magnitude higher than the ozone concentration in the daytime. For a full solution of this problem, however, the reaction rate should be calculated at each height.

According to Slater's investigations /114/ on the mixing effect, turbulence is still slight at altitudes above 50 km.

It may be seen from Table 1 that most of the ozone is concentrated in the lower parts of the ozone layer (5/6 of the total ozone mass is concentrated below 30 km). The photochemistry of this part of the ozone layer has recently been studied in detail by Dütsch /56/ and Paetzold /116, 122/. The photochemical theory by itself can explain only the vertical distribution of ozone above the maximum of the layer, and the existence of this maximum. In a number of important points the conclusions of the photochemical theory contradict the facts: 1) the theory predicts an increase in the ozone concentration during the summer, while the maximum is in fact found in the

spring, 2) the theory predicts an increase in the ozone concentration at low latitudes, while in fact an increase is found at high latitudes, 3) the theory predicts too much ozone just below the maximum of the layer, and does not give any explanation for the presence of ozone less than 10 km above the Earth. As has been shown above, all these difficulties are cleared up when the circulation and mixing effects in the stratosphere are taken into account.

Conclusion

The presence of a layer in the stratosphere containing a considerable concentration of ozone causes a number of atmospheric phenomena, which demand careful investigation. Recently, particularly in connection with the IGY, atmospheric ozone has again been the subject of much interest, as may be seen from the many investigations planned and the review articles recently published in many countries: USA /68, 90, 91, 106, 168/, England /103/, Germany /97, 126, 150/, France /155/, Italy /70/, Bulgaria /6/, etc.

The questions of the possibilities and demands of aviation and aviation medicine also give rise to a special interest in the ozone layer /46, 92/.

A recent detailed account "Ozone in the Earth's Atmosphere" by Paetzold and Regener /126/ pays a great deal of attention to work carried out in Germany up till 1955-1956, but completely ignores Soviet work. A large bibliography of the literature on ozone published up to 1959 has very recently been compiled by Rice and Thuronyi /139/. Nearly every paper in this list is provided with a few notes. This makes it much easier to use the published material. We shall therefore only mention briefly the investigations of some effects connected with the ozone layer which have not been discussed yet.

The strongest confirmation of the fact that there is an ozone layer at a height of about 25 km is /10, 37/ in the first place the heating of the stratosphere, with a temperature maximum at about 50 km, and secondly the "hothouse" effect of the atmosphere, i. e., the fact that the atmosphere absorbs heat radiated from the surface of the Earth. This storage of heat smooths out the daily temperature fluctuations of the Earth. It has recently been shown that the role played by ozone in the second effect is slight.

The temperature of the stratosphere has been measured using sounding balloons. A minimum of −60°C is found at about 15–20 km, and the temperature then increases, first gradually and then more rapidly, to a maximum of +10°C at 45–50 km. Up to an altitude of about 20 km a regular seasonal variation in the temperature is observed, with a maximum in July-August /65/. The amplitude of this variation decreases with height, and is about 7°C at 30 km.

The effective temperature of the ozone layer may be measured by spectrophotometry of the Huggins bands (this method was worked out and used by Barbe, Chalonge and Vassy) and from the infrared emission of ozone in the 9.6μ band (Adel). A summary of the results obtained by the first method has been given by E. and A. Vassy /153/. It is found that the ozone temperature has a clear seasonal variation (with a maximum in the summer) and a systematic daily variation. According to measurements at Wassenaar in November 1953 /124, 169/, the effective temperature of the ozone layer was −35 ± 2°C, which corresponds to a height of about 30 km. Similar

measurements have confirmed the assumption that the increase of the temperature in the stratosphere is due to absorption of the ultraviolet radiation from the Sun by the ozone, but so far the cooling mechanism and the temperature variation in the stratosphere have not been explained.

Johnson calculated the heating of ozone at various altitudes as a result of the absorption of solar radiation (the results are given in /17/) and the daily temperature variation resulting from this. Similar calculations were later carried out in Japan by Horiuchi /77/, who found one temperature maximum at 42 km and a second at 65 km. Johnson, Purcell and Tousey showed /17/ that ozone is apparently not the main radiator in the thermal region of the stratosphere, since the calculated maximum of the cooling and of the temperature variation is at a much higher altitude than the observed maximum of the ozone layer and nearly coincides with the temperature maximum. This shows that the source of radiation must be a gas which is present at constant relative concentration in the atmosphere, and is most likely to be water vapor or carbon dioxide.

Craig and Ohring /52/ and Ohring /114/ have carried out a great deal of calculations on the change in temperature with latitude at various altitudes and at different times throughout the whole year. Ohring /114/ showed that the cooling of the atmosphere is mainly caused by CO_2, not H_2O and much less by ozone. Brooks /48/ came to similar results. Heat flow into the stratosphere is due to infrared radiation in the 9.6μ ozone band. The heating of the atmosphere in the ozone layer is mainly due to absorption of solar ultraviolet radiation by the ozone molecules; but at higher temperatures the amount of ozone and hence the heating effect decreases, thus giving a fairly stable equilibrium in the ozone layer /52/.

In particular, the problem of the temperature and cooling of ozone up to an altitude of 50 km has recently been studied by Epstein and Adel /64/. They confirmed that the cooling of the atmosphere by ozone radiating in the 9.6μ band is negligible below 5–6 km, while at an altitude of about 45 km the cooling reaches 3° per day in the summer. The altitude of maximum heating varies throughout the year from 18 km–25 km in the summer.

Similarly, Attmannspacher /40/ showed that up to 20 km the atmosphere is heated by the Earth, while at higher altitudes the heating comes from the ozone layer.

The presence of ozone in the atmosphere also determines the brightness and color of the sky, or its spectrum, to a certain extent /80/. The spectrum of the sky shows a slight minimum in the region of $\lambda = 5400$ Å, which is attributed to absorption by ozone in the Chappuis band. At twilight, the strong absorption in the ozone layer makes the sky appreciably bluer, which has been confirmed by Gadsden /69/. Further calculations on the amount of radiation in the atmosphere absorbed in the ultraviolet and infrared ozone bands have been carried out by Dave and Sekera /53/. The authors calculated for various wavelengths the effect of changes in the ozone content, the turbidity of the atmosphere, the Earth's albedo and the height of the Sun above the horizon. The calculated values are in good agreement with experiment.

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LIST OF ABBREVIATIONS

Abbreviation	Full name (transliterated)	Translation
AN SSSR	Akademiya nauk SSSR	Academy of Sciences U. S. S. R.
GGO	Glavnaya geofizicheskaya observatoriya	The Main Geophysical Observatory
GONTI	Gosudarstvennoe ob"edinennoe nauchno-tekhnicheskoe izdatel'svo	The State Joint Scientific-Technical Publishing House
GITTI	Gosudarstvennoe izdatel'stvo tekhniko-teoreticheskoi literatury	The State Publishing House of Technical-Theoretical Literature
Kaz NIGMI	Kazakhskii nauchno-issledovatel'skii gidrometeorologicheskii institut	Kazakh Hydrometeorological Scientific Research Institute
UFN	Uspekhi fizicheskikh nauk	Progress of Physical Sciences
ZhTF	Zhurnal tekhnicheskoi fiziki	Journal of Technical Physics